

Supporting Information

# Tetranuclear Copper Complexes with Bulky Aminoalcohol Ligands as Catalysts for Oxidative Phenoxazinone Synthase-like Coupling of Aminophenol: A Combined Experimental and Theoretical Study

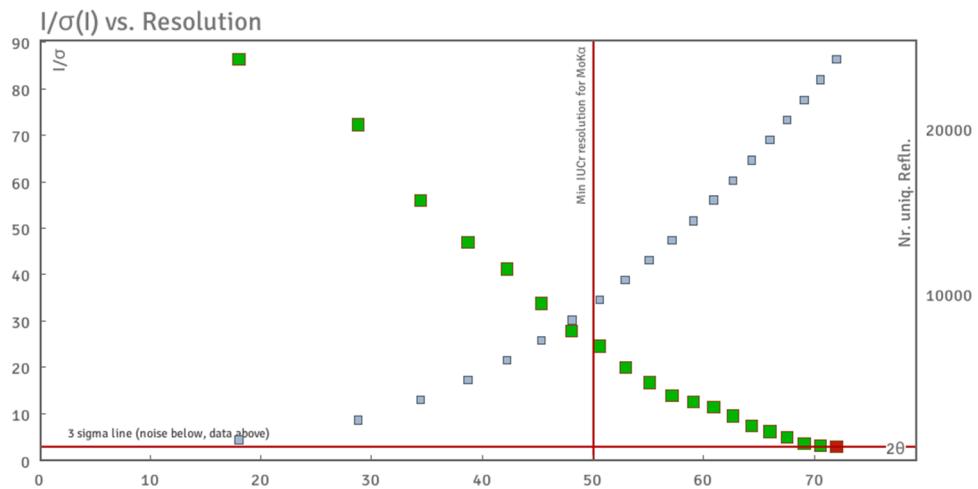
Oksana V. Nesterova, Armando J. L. Pombeiro and Dmytro S. Nesterov \*

Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico,  
Universidade de Lisboa, 1049-001 Lisbon, Portugal

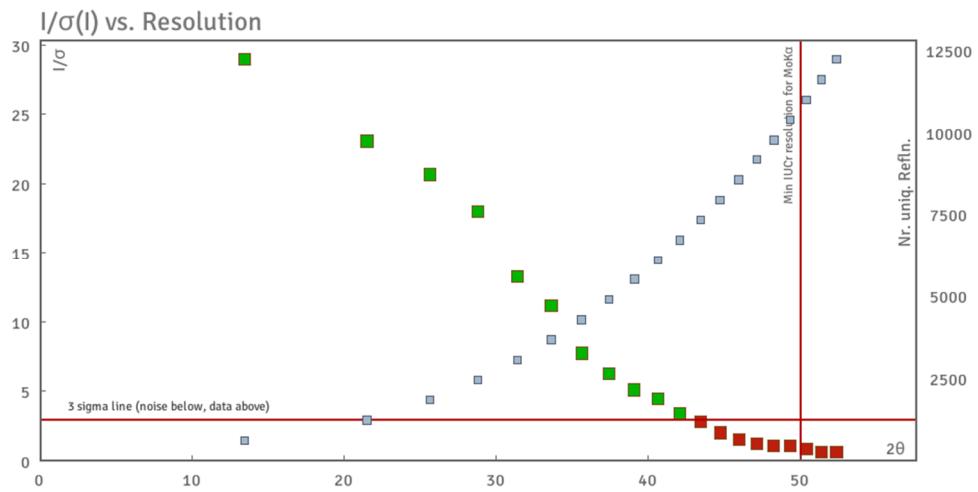
\* Correspondence: dmytro.nesterov@tecnico.ulisboa.pt

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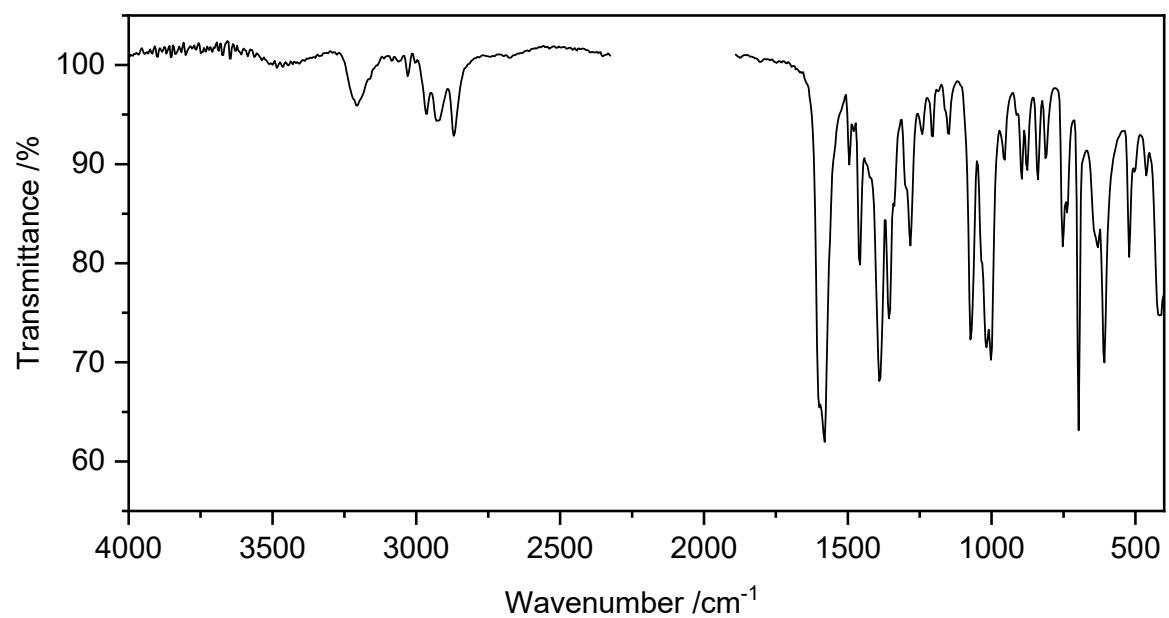
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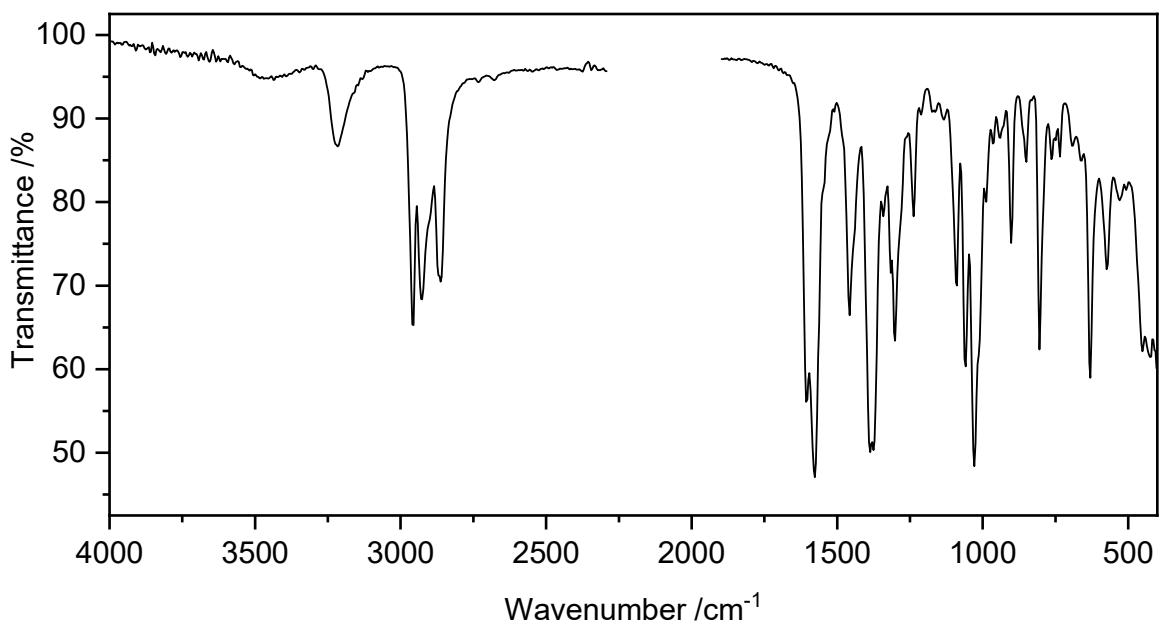
**Figure S1.** Reflection intensity statistics ( $I/\sigma(I)$  vs.  $2\theta$ ) for **1**.



**Figure S2.** Reflection intensity statistics ( $I/\sigma(I)$  vs.  $2\theta$ ) for **2**.



**Figure S3.** IR spectrum of **1**.



**Figure S4.** IR spectrum of **2**.

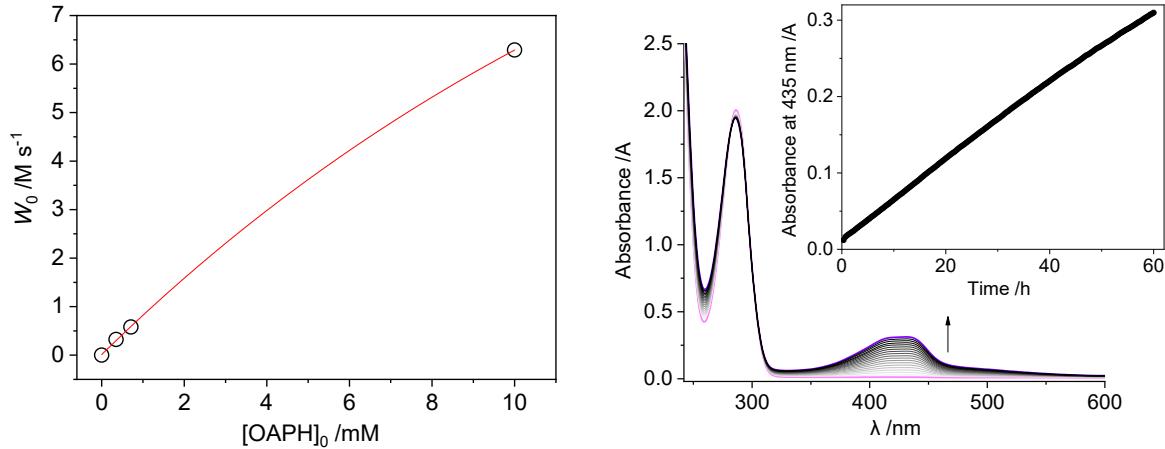
**Table S1.** Crystal data and structure refinement for **1** and **2**.

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>48</sub> H <sub>70</sub> Cu <sub>4</sub> N <sub>4</sub> O <sub>13</sub>	C <sub>48</sub> H <sub>102</sub> Cu <sub>4</sub> N <sub>4</sub> O <sub>13</sub>
Formula weight	1165.24	1197.49
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> bca
<i>a</i> /Å	14.9714(12)	24.9398(17)
<i>b</i> /Å	20.5967(17)	17.2093(11)
<i>c</i> /Å	16.9773(12)	29.0333(19)
$\alpha/^\circ$	90	90
$\beta/^\circ$	95.402(3)	90
$\gamma/^\circ$	90	90
<i>V</i> /Å <sup>3</sup>	5211.9(7)	12461.0(14)
<i>Z</i>	4	8
Calculated density/g cm <sup>-3</sup>	1.485	1.277
<i>T</i> , K	150	150(2)
$\mu$ (Mo-K <sub>α</sub> )/mm <sup>-1</sup>	1.674	1.402
<i>F</i> (000)	2424	5104
Reflections collected/unique	322320/25120	118990/12791
<i>R</i> <sub>int</sub>	0.0512	0.1184
Reflections with <i>I</i> > 2σ( <i>I</i> )	19107	6493
$\Theta_{\min}, \Theta_{\max}/^\circ$	1.997, 36.351	2.009, 26.431
<i>R</i> <sub><i>I</i></sub> , <i>I</i> > 2σ( <i>I</i> )	0.0353	0.0759
<i>wR</i> <sub>2</sub> (all data)	0.0763	0.2601
<i>GoF</i>	1.048	1.045

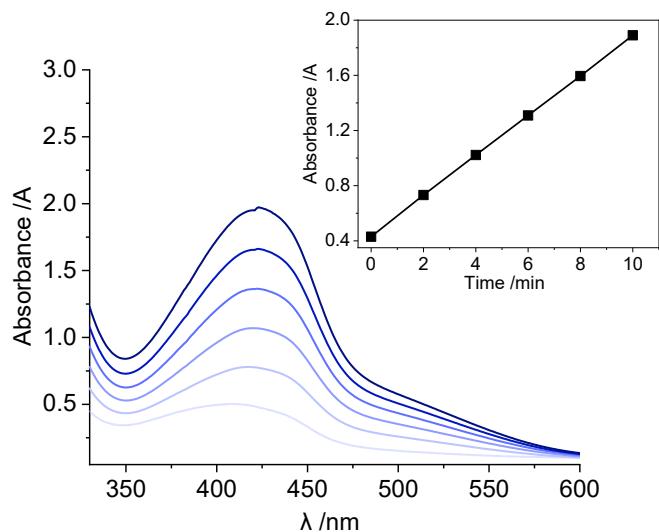
**Table S2.** Selected geometrical parameters (distances/Å and angles/°) for **1** and **2**.

	<b>1</b>	<b>2</b>
Cu1–O1	1.9645(9)	1.956(4)
Cu1–O2	1.9495(9)	1.925(5)
Cu1–O4	1.9602(8)	1.978(5)
Cu1–O10	2.3522(8)	2.403(4)
Cu1–N1	2.0337(10)	2.019(6)
Cu2–O1	1.9646(8)	1.959(5)
Cu2–O4	1.9754(9)	1.955(4)
Cu2–O5	1.9577(9)	1.928(5)
Cu2–O7	2.5784(9)	2.402(4)
Cu2–N2	2.0153(10)	2.024(6)
Cu3–O1	2.3769(8)	2.531(4)
Cu3–O7	1.9374(9)	1.958(4)
Cu3–O8	1.9181(10)	1.905(5)
Cu3–O10	2.0025(9)	1.977(4)
Cu3–N3	2.0359(11)	2.025(6)
Cu4–O4	2.3386(8)	2.411(4)
Cu4–O7	1.9479(9)	1.981(4)
Cu4–O10	1.9754(9)	1.960(4)
Cu4–O11	1.9353(10)	1.931(5)
Cu4–N4	2.0132(11)	2.007(6)
O1–Cu1–O4	82.60(4)	82.47(19)
O1–Cu1–O10	80.89(3)	81.77(16)
O1–Cu1–N1	85.42(4)	85.1(2)
O2–Cu1–O1	175.73(4)	176.6(2)
O2–Cu1–O4	97.81(4)	94.7(2)
O2–Cu1–O10	103.38(3)	99.77(18)
O2–Cu1–N1	93.34(4)	97.2(2)
O4–Cu1–O1	82.60(3)	82.47(19)
O4–Cu1–O10	81.01(3)	80.23(16)
O4–Cu1–N1	163.87(4)	162.7(2)
N1–Cu1–O10	107.73(4)	109.9(2)
O1–Cu2–O7	76.04(3)	79.31(16)
O1–Cu2–O4	82.22(3)	82.98(18)
O1–Cu2–N2	165.93(4)	161.5(2)
O4–Cu2–O1	82.22(3)	82.98(18)
O4–Cu2–O7	74.12(3)	81.31(16)
O4–Cu2–N2	84.46(4)	83.9(2)
O5–Cu2–O1	95.77(4)	95.7(2)
O5–Cu2–O4	177.14(4)	178.6(2)
O5–Cu2–O7	103.45(3)	98.29(18)
O5–Cu2–N2	97.70(4)	97.5(2)
N2–Cu2–O7	104.58(4)	111.5(2)
O7–Cu3–O1	81.63(3)	76.10(16)
O7–Cu3–O10	82.77(4)	82.52(18)
O7–Cu3–N3	84.37(4)	84.5(2)

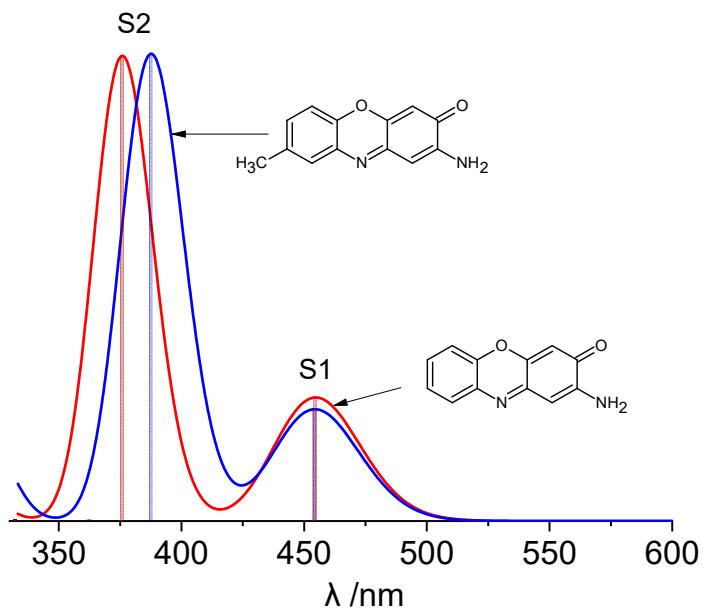
O8–Cu3–O1	98.46(3)	100.57(18)
O8–Cu3–O7	179.45(4)	175.8(2)
O8–Cu3–O10	96.71(4)	94.4(2)
O8–Cu3–N3	96.11(5)	99.3(2)
O10–Cu3–O1	79.52(3)	78.10(15)
O10–Cu3–N3	164.20(4)	159.7(2)
N3–Cu3–O1	107.63(4)	113.75(19)
O7–Cu4–O4	80.52(3)	80.56(15)
O7–Cu4–O10	83.21(4)	82.36(18)
O7–Cu4–N4	164.10(4)	164.0(2)
O10–Cu4–O4	81.05(3)	80.34(16)
O10–Cu4–O7	83.21(4)	82.36(18)
O10–Cu4–N4	84.96(4)	85.1(2)
O11–Cu4–O4	101.82(3)	99.75(18)
O11–Cu4–O7	92.30(4)	94.6(2)
O11–Cu4–O10	174.25(4)	176.9(2)
O11–Cu4–N4	98.75(4)	97.9(2)
N4–Cu4–O4	108.08(4)	107.1(2)



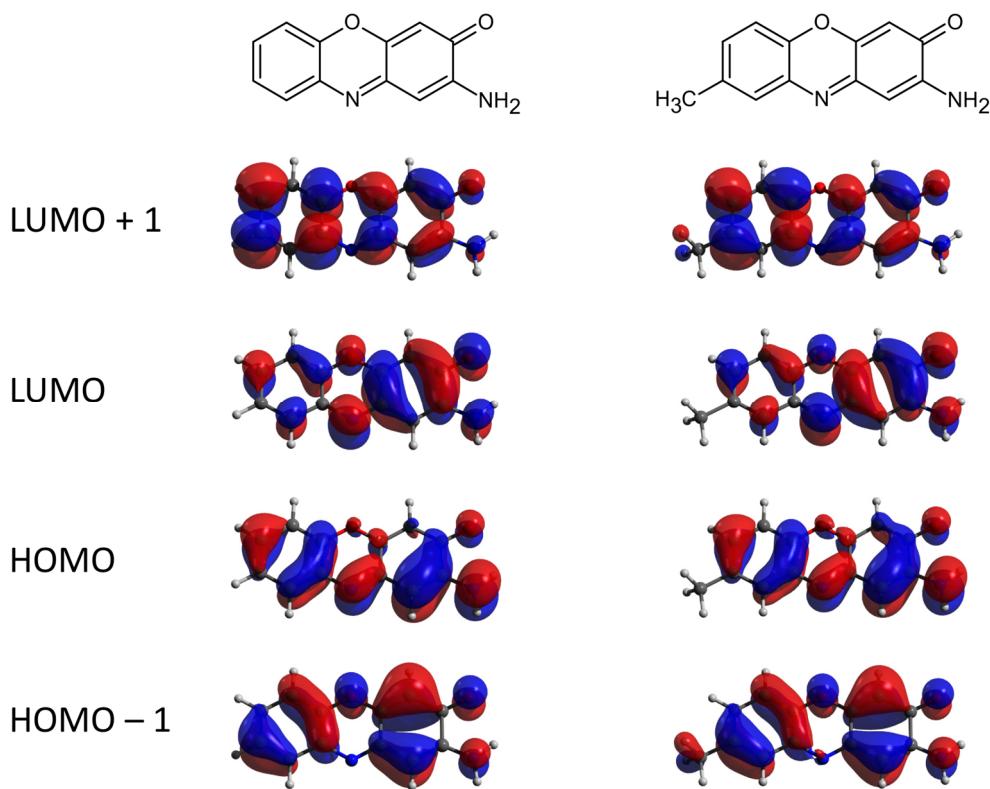
**Figure S5.** Left: dependence of the initial reaction rate  $W_0$  on the OAPH concentration in the catalyst-free aerobic oxidation of OAPH in methanol at room temperature. Right: change of the UV/Vis spectra for  $[\text{OAPH}]_0 = 7.4 \times 10^{-4} \text{ M}$ . The inset shows increase of the band at 435 nm.



**Figure S6.** Increase of the band at 435 nm, attributable to the phenoxazinone chromophore (PCXR), over time in the aerobic oxidation of the mixture of *o*-aminophenol (OAPH, 10 mM) and 2-amino-*p*-cresol (10 mM) catalysed by **1** (0.4 mM) in methanol. The inset shows the evolution of the 435 nm absorption with time.



**Figure S7.** Fragment of the TD-DFT calculated absorption spectra of the normal and methyl-substituted phenoxazinone chromophores. The absorptions corresponding to the first two strongest excitation states S1 and S2 are shown (absorption wavelengths are stated in the Listings S1 and S2). TD-DFT calculations were performed at the PBE0/ma-def2-TZVPP level for the B3LYP/ma-def2-TZVP optimized geometries in methanol. Only singlet excitations were considered. *VeryTightSCF* and *Defgrid3* keywords were used for the SCF convergence criteria and the integration grids.



**Figure S8.** Frontier molecular orbitals of the normal and methyl-substituted phenoxazinone chromophores (PBE0/ma-def2-TZVPP TD-DFT calculation using B3LYP/ma-def2-TZVP geometry in methanol; only singlet excitations were considered).

**Listing S1.** Fragment of the ORCA output for the TD-DFT calculation of the phenoxazinone chromophore (**54a** = HOMO and **55a** = LUMO orbitals). The numbers after the transition indicate the contributions of the respective transitions to excited states.

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STATE 1: E= 0.100198 au  2.727 eV  21990.9 cm**-1 <S**2> =  0.000000  454.7 nm
 53a -> 55a :  0.369243 (c= -0.60765395)
 54a -> 55a :  0.584070 (c= -0.76424447)
STATE 2: E= 0.121203 au  3.298 eV  26601.0 cm**-1 <S**2> =  0.000000  375.9 nm
 53a -> 55a :  0.586840 (c=  0.76605463)
 53a -> 56a :  0.024133 (c=  0.15534867)
 54a -> 55a :  0.326698 (c= -0.57157530)
 54a -> 56a :  0.017738 (c=  0.13318325)

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ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS  
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State	Energy (cm <sup>-1</sup> )	Wavelength (nm)	fosc (au <sup>**2</sup> )	T2 (au)	TX (au)	TY (au)	TZ (au)
1	21990.9	454.7	0.213737528	3.19973	-1.78797	0.00783	-0.05319
2	26601.0	375.9	0.804819675	9.96039	-3.15493	0.00193	-0.08249

**Listing S2.** Fragment of the ORCA output for the TD-DFT calculation of the methyl-substituted phenoxyazinone chromophore (**58a** = HOMO and **59a** = LUMO orbitals). The numbers after the transition indicate the contributions of the respective transitions to excited states.

STATE 1: E= 0.100269 au 2.728 eV 22006.5 cm\*\*-1 <S\*\*2> = 0.000000 **454.4 nm**

56a -> 59a : 0.015027 (c= -0.12258294)

57a -> 59a : 0.464896 (c= 0.68183313)

58a -> 59a : 0.484143 (c= 0.69580379)

STATE 2: E= 0.117531 au 3.198 eV 25795.1 cm\*\*-1 <S\*\*2> = 0.000000 **387.7 nm**

57a -> 59a : 0.498659 (c= -0.70615767)

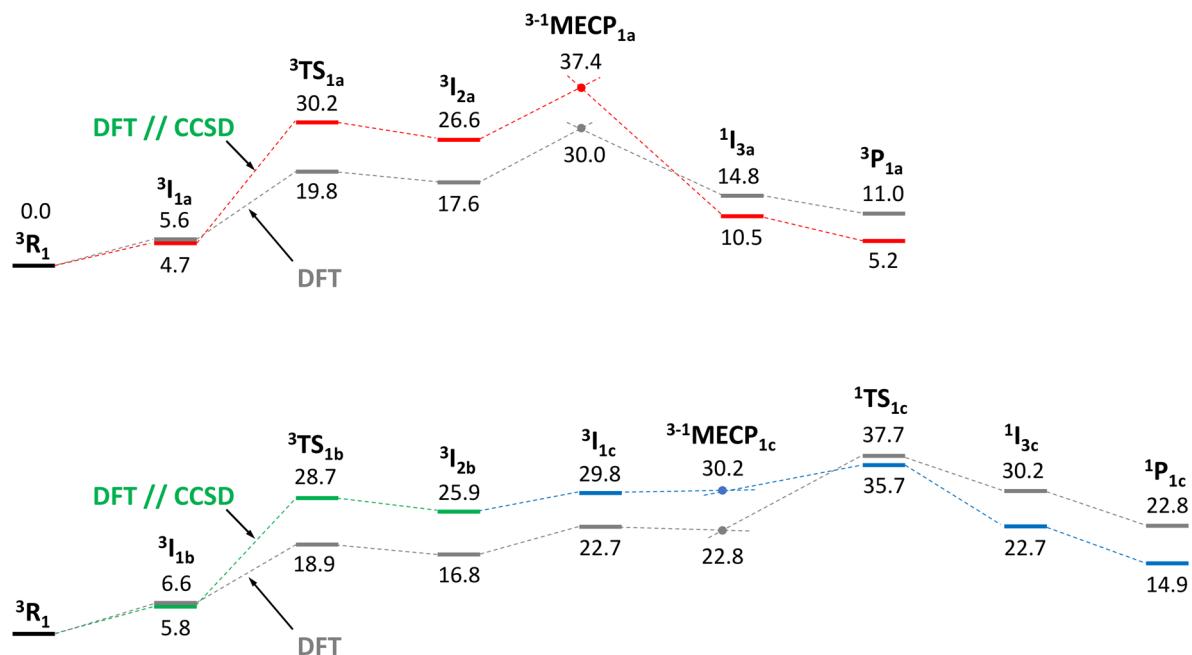
57a -> 60a : 0.021822 (c= 0.14772195)

58a -> 59a : 0.416546 (c= 0.64540383)

58a -> 60a : 0.012209 (c= 0.11049409)

#### ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy (cm <sup>-1</sup> )	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)		TZ (au)
1	22006.5	454.4	0.193388698	2.89304	-1.70017	0.00581	-0.04943
2	25795.1	387.7	0.808556071	10.31928	-3.20902	0.06230	-0.13266

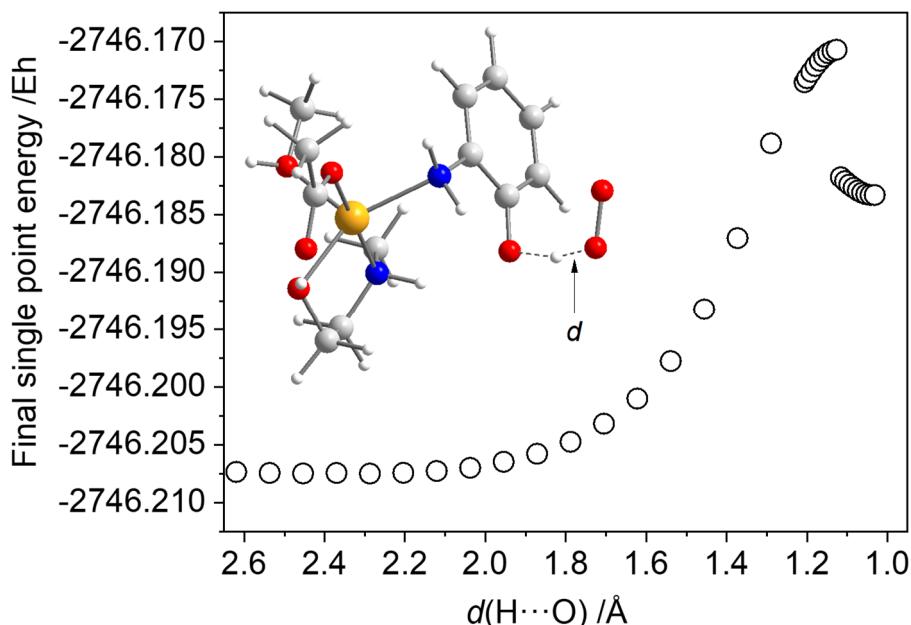


**Scheme S1.** Comparison of free energy profiles for the aerobic oxidation of OAPH (R = reactant, I = intermediate, TS = transition state, P = product, MECP = minimum energy crossing point) calculated at the B3LYP/ma-def2-TZVP (**DFT**) and B3LYP/ma-def2-TZVP // DLPNO-CCSD(T)/ma-def2-TZVPP (**DFT // CCSD**) levels. The numbers show the change of the free Gibbs energy,  $\Delta G$  (kcal mol<sup>-1</sup>), relative to the starting reactant <sup>3</sup>R<sub>1</sub>.

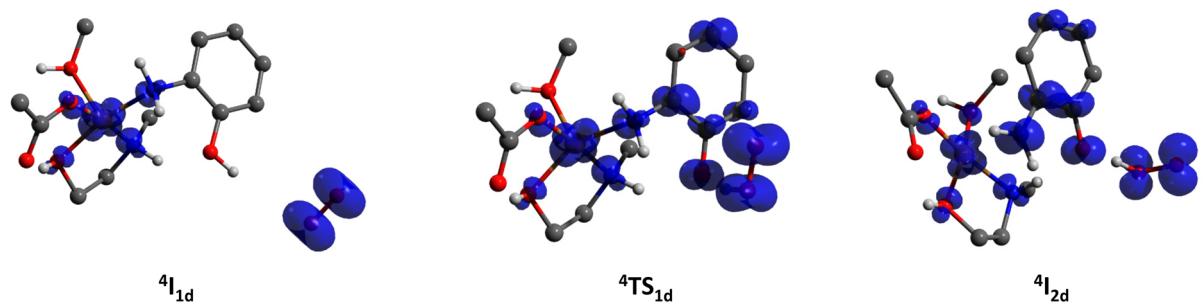
**Table S3.** Comparison of the barriers between  $^3\text{TS}_{1\text{a}}$  and  $^3\text{I}_{1\text{a}}$  states calculated at different theory levels.

Run	Method	Basis set	Integration grid <sup>a</sup>	Solvation model <sup>b</sup>	$\Delta G^c$ , kcal mol <sup>-1</sup>
1 <sup>d</sup>	B3LYP	ma-def2-TZVP	Defgrid2	C-PCM	14.3
2 <sup>e</sup>	DLPNO-CCSD(T)	ma-def2-TZVPP	–	SMD	25.5
3	B3LYP	ma-def2-TZVP	Defgrid2	C-PCM	13.7
4	B3LYP	ma-def2-TZVP	Defgrid3	C-PCM	13.7
5	B3LYP	ma-def2-TZVP	Defgrid3	SMD	13.5
6	B3LYP	ma-def2-TZVPP	Defgrid3	SMD	13.6
7	$\omega$ B97X	ma-def2-TZVPP	Defgrid3	SMD	20.4
8	B2PLYP	ma-def2-TZVPP	Defgrid3	SMD	20.3
9 <sup>f</sup>	B3LYP	ma-def2-TZVP	Defgrid3	SMD	14.3
10 <sup>g</sup>	DLPNO-CCSD(T)	ma-def2-TZVPP	–	SMD	26.4

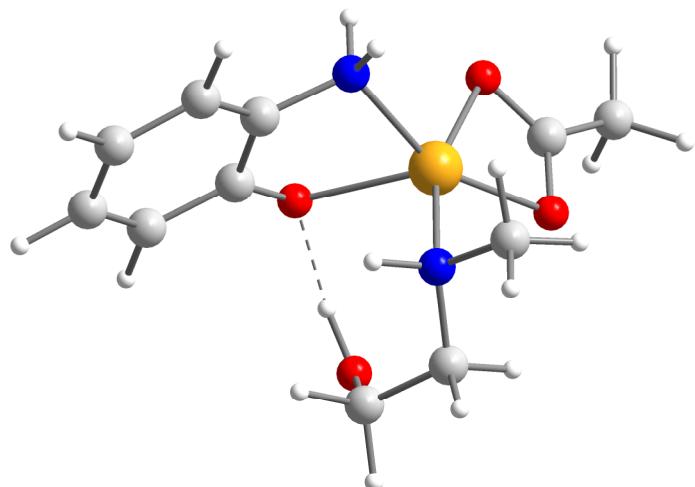
<sup>a</sup> the keyword used to generate the integration grids (Defgrid2 is default in ORCA 5.0.3); <sup>b</sup> solvation model used for calculation of the geometry and energies (DFT) or single point energy (CCSD); <sup>c</sup>  $\Delta G = G_{\text{TS}} - G_{\text{I}}$ , where  $G = G_{\text{DFT}} - E_{\text{DFT}} + E_{\text{selected method}}$  and  $E_{\text{selected method}}$  is the single point electronic energy calculated at the chosen level. The molecular geometries and  $G_{\text{DFT}} - E_{\text{DFT}}$  contributions obtained from the run 1 were used, unless stated otherwise. The SCF convergence criteria were settled by *VeryTightSCF* keyword, unless stated otherwise; <sup>d</sup> The entry corresponds to that shown in the Scheme S1. *TightSCF* convergence criteria were used; <sup>e</sup> the run corresponds to the results shown in Schemes 4 and S1; <sup>f</sup> geometries re-optimized at  $G_{\text{DFT}} - E_{\text{DFT}}$  values re-calculated at the respective level. Numerical frequency calculations were invoked with *NumFreq* keyword; <sup>g</sup> molecular geometries and  $G_{\text{DFT}} - E_{\text{DFT}}$  values from the run 9 were used.



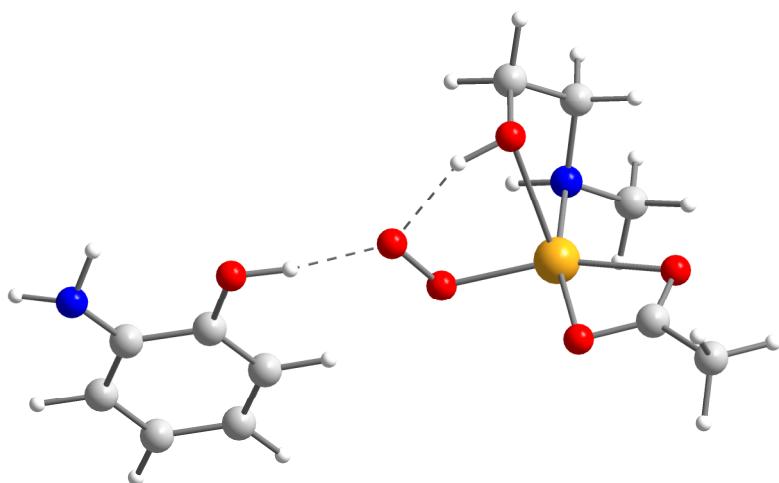
**Figure S9.** Relaxed energy scan along the transition state coordinate for the H-atom abstraction from OAPH catalysed by the  $[\text{Cu}^{II}(\text{HMeEa})(\text{OAc})(\text{MeOH})]^+$  complex. The final point at the 1.031 Å corresponds to the optimized geometry of the reaction product  $^4\text{I}_{2\text{d}}$ , while the respective separation in the reactant  $^4\text{I}_{1\text{d}}$  configuration constitutes 3.046 Å. The figure shows the transition state  $^4\text{TS}_{1\text{d}}$ . Colour scheme: Cu, orange; O, red; N, blue; C, grey; H, white.



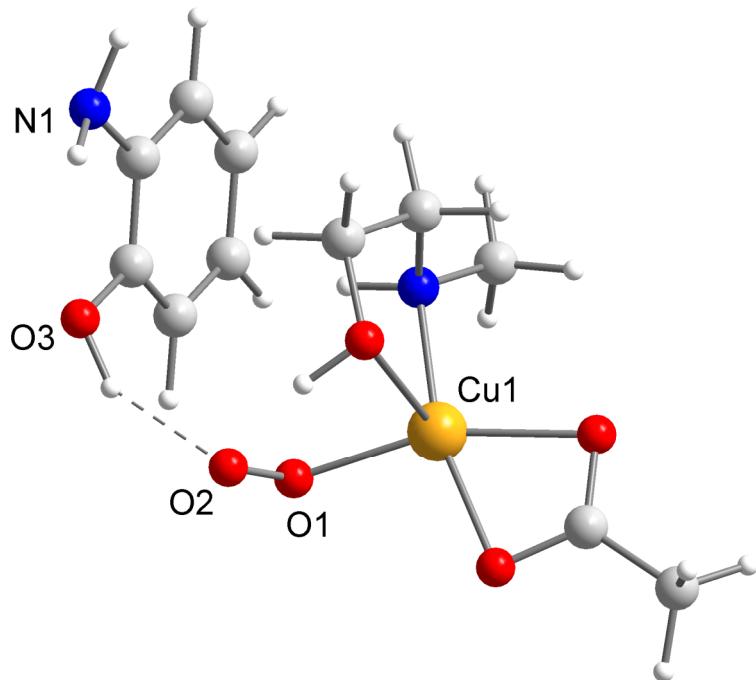
**Figure S10.** Isosurfaces of the spin density (0.01 a.u. level) for the optimized intermediates  $^4\text{I}_{1\text{d}}$ ,  $^4\text{I}_{2\text{d}}$  and transition state  $^4\text{TS}_{1\text{d}}$ . Hydrogen atoms of the C–H groups are omitted for clarity. Colour scheme: Cu, orange; O, red; N, blue; C, grey; H, white.



**Figure S11.** DFT optimized structure of the  $[\text{Cu}^{\text{II}}(\text{HMeEa})(\text{OAc})(\text{OAP})]$  complex, where OAP ligand is in the deprotonated state. Colour scheme: Cu, orange; O, red; N, blue; C, grey; H, white.



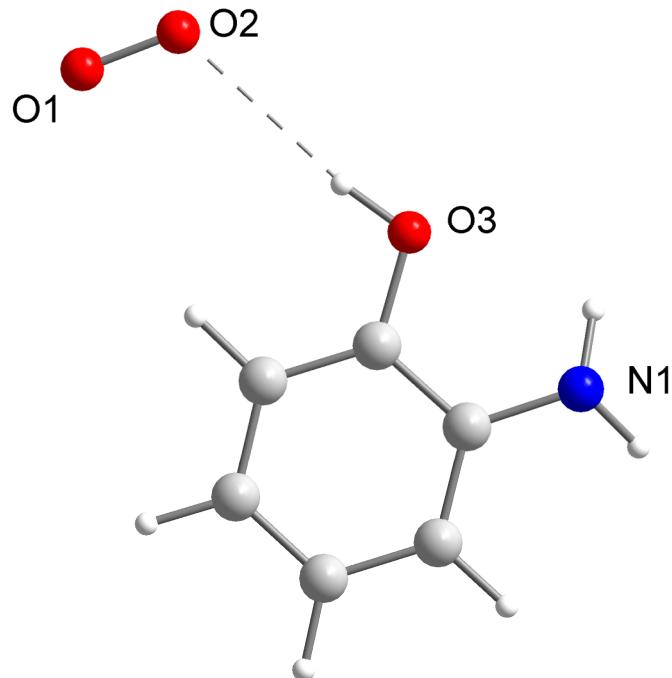
**Figure S12.** DFT optimized structure of the  ${}^3\text{I}_{\text{ea}}$  intermediate. Colour scheme: Cu, orange; O, red; N, blue; C, grey; H, white.



**Figure S13.** DFT optimized structure of the  ${}^3\text{I}_{1\text{e}}$  intermediate with partial numbering scheme. Colour scheme: Cu, orange; O, red; N, blue; C, grey; H, white.

**Table S4.** Löwdin spin population and atomic charges for selected atoms in  ${}^3\text{I}_{1\text{e}}$  (Figure S13).

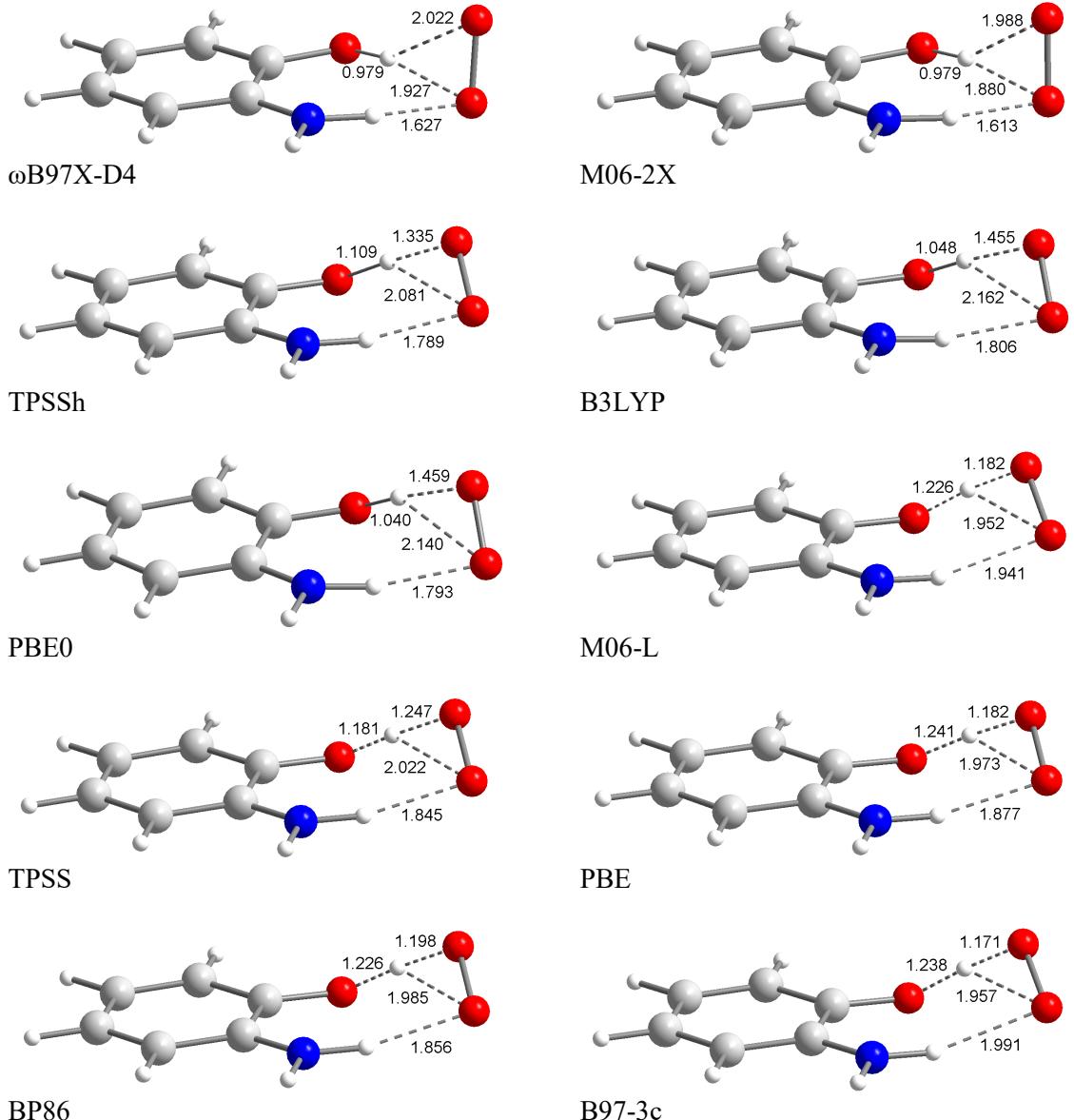
Atom	Reactant	TS	Product
Spin polulation			
Cu	0.579226	0.600253	0.600674
O1	0.613414	0.427286	0.169177
O2	0.570824	0.253186	0.026249
O3	0.009526	0.132238	0.215509
N1	0.000392	0.090502	0.194386
Charge			
Cu	0.171570	0.171459	0.171961
O1	-0.137042	-0.218458	-0.339458
O2	-0.241359	-0.234992	-0.227434
O3	-0.044145	-0.072181	-0.097974
N1	-0.110180	-0.026488	0.045216



**Figure S14.** DFT optimized structure of the  $^3\text{I}_{1\text{b}}$  intermediate with partial numbering scheme. Colour scheme: Cu, orange; O, red; N, blue; C, grey; H, white.

**Table S5.** Löwdin spin population and atomic charges for selected atoms in  $^3\text{I}_{1\text{b}}$  (Figure S14).

Atom	Reactant	TS	Product
Spin population			
O1	1.004912	0.679041	0.658477
O2	0.992571	0.532826	0.342151
O3	0.001430	0.119813	0.199846
N1	0.000017	0.195019	0.206277
Charge			
O1	0.006290	-0.263619	-0.229089
O2	-0.004307	-0.246195	-0.112745
O3	-0.033520	0.007477	-0.083656
N1	-0.118025	0.059955	0.053885

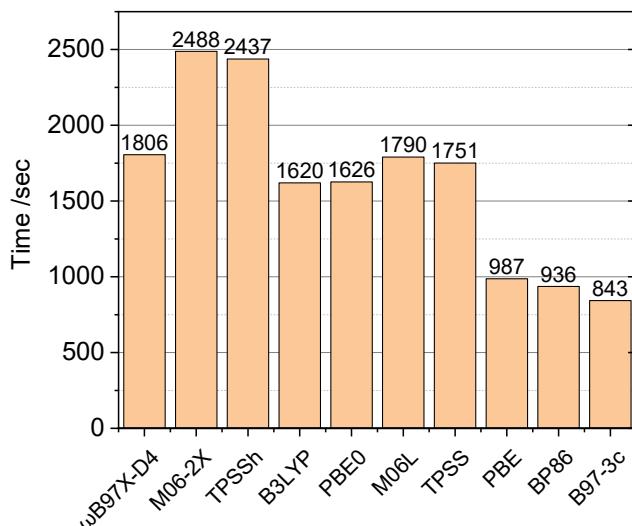


**Figure S15.** Molecular geometries and selected interatomic distances ( $\text{\AA}$ ) for the  ${}^3\text{TS}_{1a}$  transition state optimized using different functionals. In all cases the new transitions states were found through the complete NEB-TS search between  ${}^3\text{I}_{1a}$  and  ${}^3\text{I}_{2a}$  intermediates using the respective functionals. Other conditions: ma-def2-TZVP basis set, *Defgrid3* keyword for integration grids, *VeryTightSCF* and *SlowConv* keywords for SCF convergence criteria. Dispersion corrections were introduced using *D3Zero* (for M06-L and M06-2X functionals), *D3BJ* (for B97-3c functional) and *D4* (for other functionals) keywords.

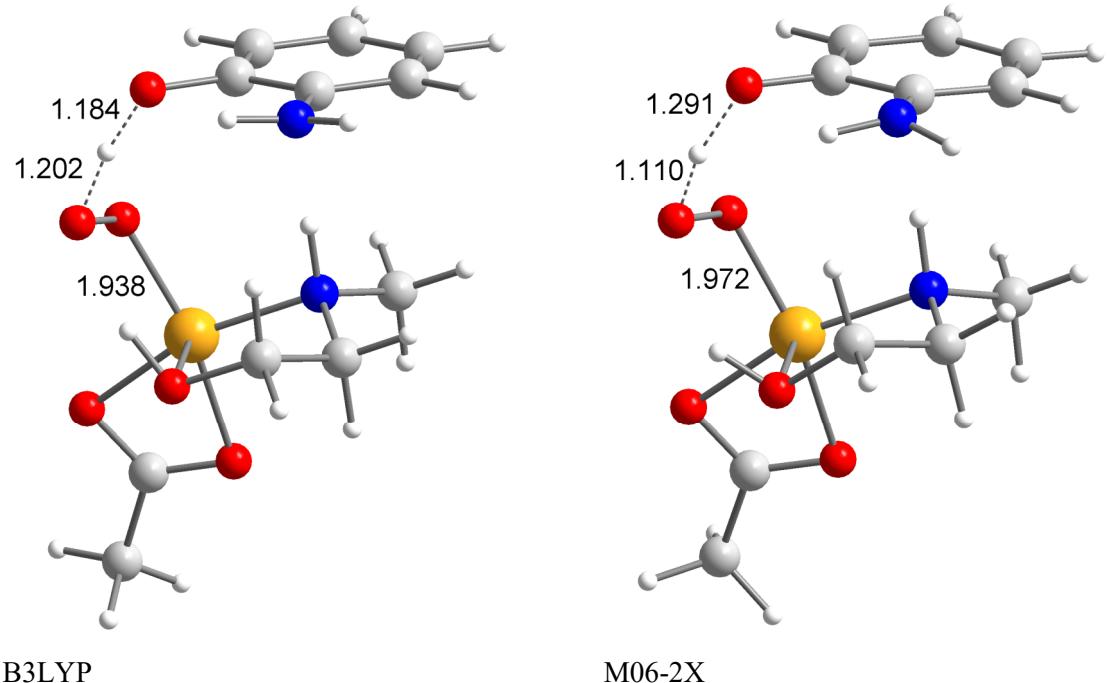
**Table S6.** Gibbs energies of  $^3\text{TS}_{1\text{a}}$  and  $^3\text{I}_{2\text{a}}$  states relative to  $^3\text{I}_{1\text{a}}$  one obtained using indicated DFT functionals before or after correction of electronic energies at the DLPNO-CCSD(T) level.<sup>a</sup>

Functional		$\Delta G \ ^3\text{TS}_{1\text{a}} \ ^b$		$\Delta G \ ^3\text{I}_{2\text{a}} \ ^c$		%E(el) <sup>d</sup>
Class	Name	DFT	CCSD <sup>e</sup>	DFT	CCSD <sup>e</sup>	
range-separated hybrid GGA	wB97X-D4	29.2	34.2	17.6	21.7	81
hybrid meta-GGA	M06-2X	30.0	29.4	18.5	20.6	90
hybrid meta-GGA	TPSSh	13.5	24.6	13.0	22.3	58
hybrid GGA	B3LYP	13.5	24.5	11.2	20.8	54
hybrid GGA	PBE0	17.4	24.9	14.7	20.5	72
meta-GGA	M06-L	13.8	21.5	14.3	19.8	72
meta-GGA	TPSS	8.3	22.7	9.3	21.2	44
GGA	PBE	7.9	22.1	9.9	21.3	46
GGA	BP86	6.8	22.1	8.7	21.3	41
GGA composite	B97-3c	12.9	22.3	15.0	21.1	71

<sup>a</sup> Geometries of  $^3\text{I}_{1\text{a}}$ ,  $^3\text{I}_{2\text{a}}$  and  $^3\text{TS}_{1\text{a}}$  were optimized using the conditions described in the Figure S15 caption, except of *TightOPT* convergence criterium used for  $^3\text{I}_{1\text{a}}$  and  $^3\text{I}_{2\text{a}}$ ; <sup>b</sup>  $\Delta G = G_{^3\text{TS}_{1\text{a}}} - G_{^3\text{I}_{1\text{a}}}$ , kcal mol<sup>-1</sup>; <sup>c</sup>  $\Delta G = G_{^3\text{I}_{2\text{a}}} - G_{^3\text{I}_{1\text{a}}}$ , kcal mol<sup>-1</sup>; <sup>d</sup> Percentage of the Gibbs energy obtained at the DFT level from the Gibbs energy after DLPNO-CCSD(T) correction:  $\Delta G(\text{DFT}) / \Delta G(\text{DFT} // \text{DLPNO-CCSD(T)}) \times 100$ ; <sup>e</sup> Gibbs energy after correction of the electronic energy of all geometries at the DLPNO-CCSD(T) level:  $\Delta G = G_{\text{DFT}} - E_{\text{DFT}} + E_{\text{DLPNO-CCSD(T)}}$ . For the transition states the wavefunctions obtained from the DFT calculation were used as an initial guess for the DLPNO-CCST(T) calculations.



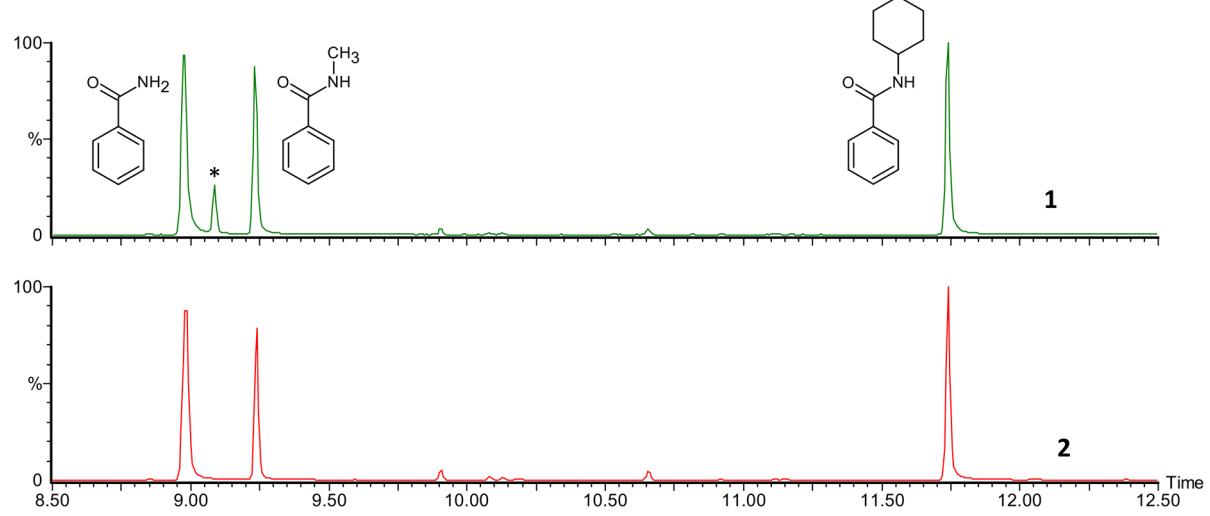
**Figure S16.** Calculation timings for single point and vibrational frequencies calculations of the  $^3\text{I}_{1\text{a}}$  intermediate using different DFT functionals. All geometries were preliminary optimized using the respective functionals. Other conditions are as follows: ma-def2-TZVP basis set, C-PCM solvent model (methanol), *VeryTightSCF* and *Defgrid3* keywords for SCF convergence and integration grids. Dispersion corrections were introduced using *D3Zero* (for M06-L and M06-2X functionals), *D3BJ* (for B97-3c functional) and *D4* (for other functionals) keywords. 4 cores (*PAL4* keyword) of the AMD Ryzen<sup>TM</sup> Threadripper<sup>TM</sup> 3960X CPU were used to exclude the possible thermal CPU throttling and reduce the multiprocessing overheads. Every core was supplied with 15 Gb of RAM (“*maxcore 15000*” command).



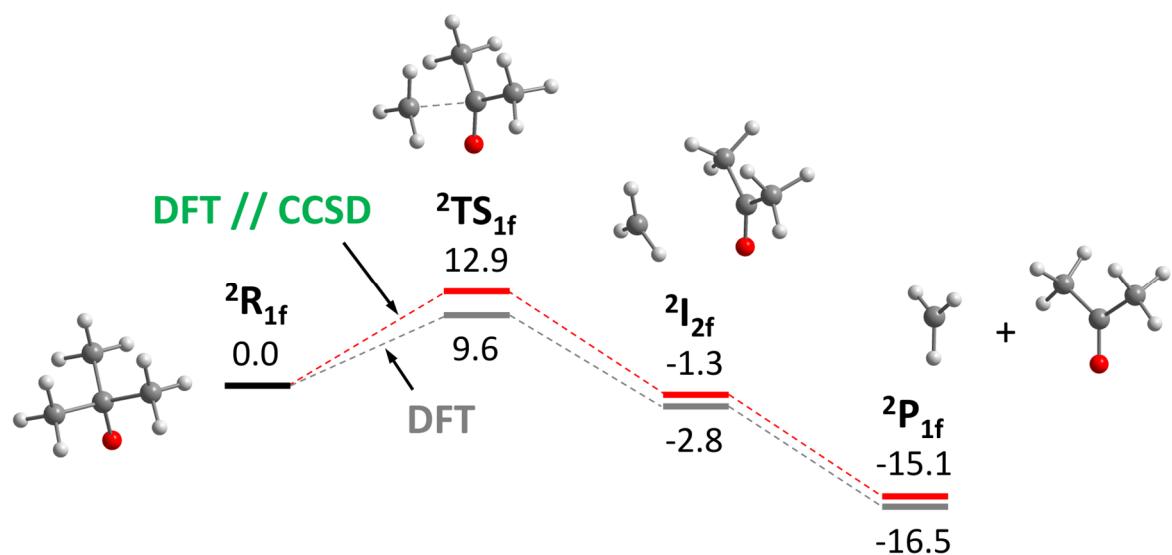
B3LYP

M06-2X

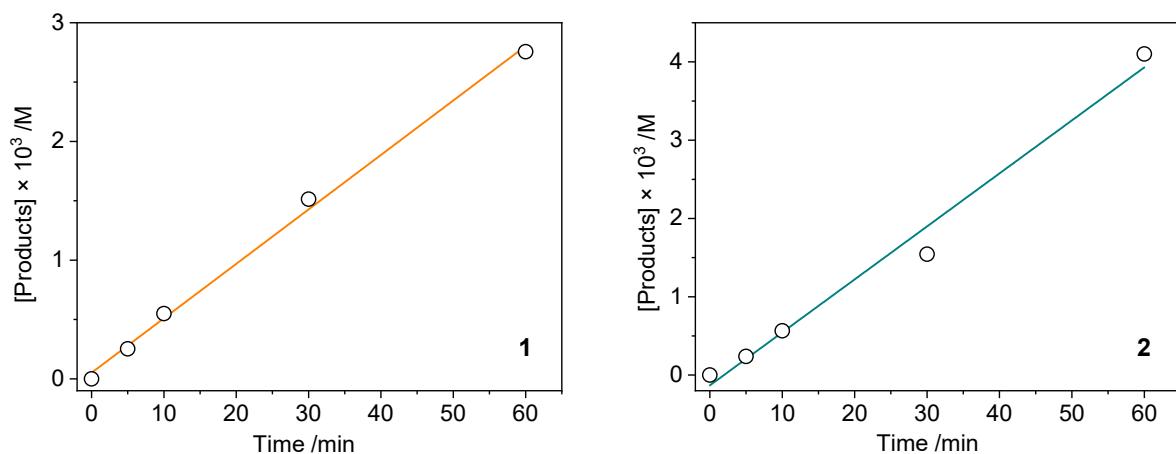
**Figure S17.** Molecular geometries and selected interatomic distances ( $\text{\AA}$ ) for the  $^3\text{TS}_{1e}$  transition state optimized using B3LYP and M06-2X functionals (ma-def2-TZVP basis set, *Defgrid3* keyword for integration grids, *VeryTightSCF* and *SlowConv* keywords for SCF convergence criteria were employed). Dispersion corrections were introduced using *D3Zero* (for M06-2X) and *D4* (for B3LYP) keywords.



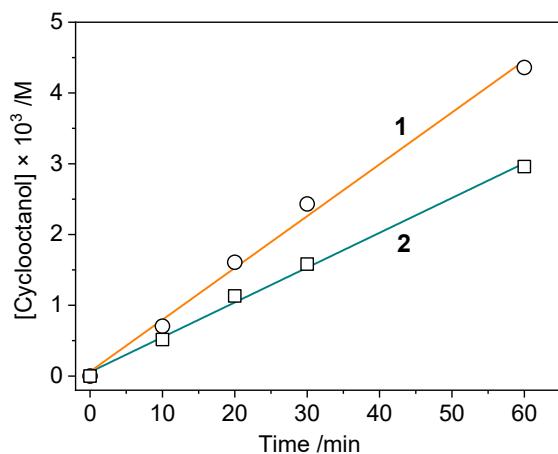
**Figure S18.** Fragments of the chromatograms (Phenomenex ZB-5 column) showing the main reaction products (as well as benzamide) in the course of oxidative cyclohexane (2.9 M) amidation with benzamide (0.3 M) in the presence of di-*tert*-butyl peroxide, DTBP (0.6 M) in chlorobenzene, catalysed by the complexes **1** (top) and **2** (bottom) (29 mM). The product \* was not identified.



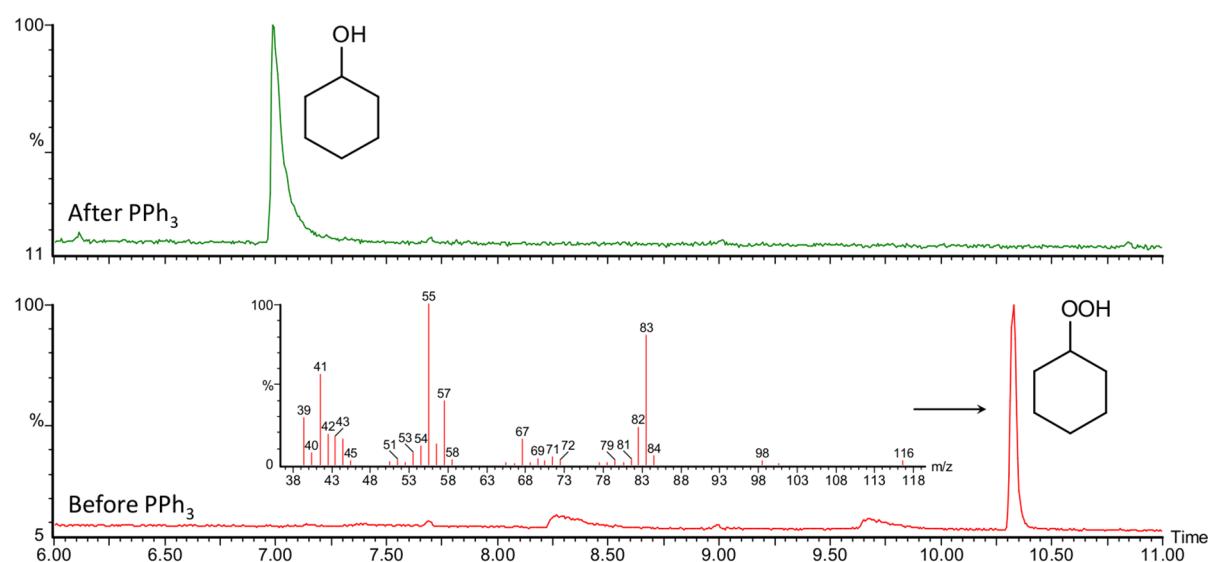
**Figure S19.** Comparison of free energy profiles for the  $\beta$ -scission of  $'\text{BuO}\cdot$  radical calculated at the B3LYP/ma-def2-TZVP (**DFT**) and B3LYP/ma-def2-TZVP // DLPNO-CCSD(T)/ma-def2-TZVPP (**DFT // CCSD**) levels at 90 °C (383.15 K) in chlorobenzene (SMD solvation model was used for all calculations). The numbers show the change of the free Gibbs energy,  $\Delta G$  (kcal mol<sup>-1</sup>), relative to the starting reactant  $^2\text{R}_{1\text{f}}$ . Colour scheme: O, red; C, grey; H, white.



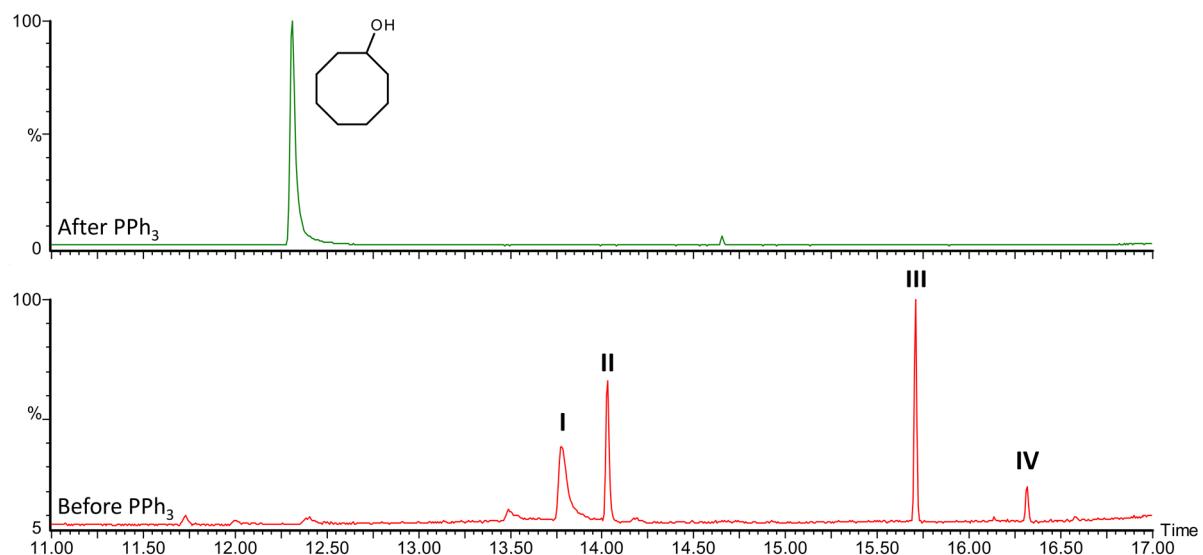
**Figure S20.** Accumulations of products (sum of cyclohexanol and cyclohexanone) in the course of cyclohexane (0.2 M) oxidation with  $\text{H}_2\text{O}_2$  (1 M) in the presence of nitric acid promoter (5 mM), catalysed by **1** (left) or **2** (right) (0.2 mM) in acetonitrile at 50 °C.



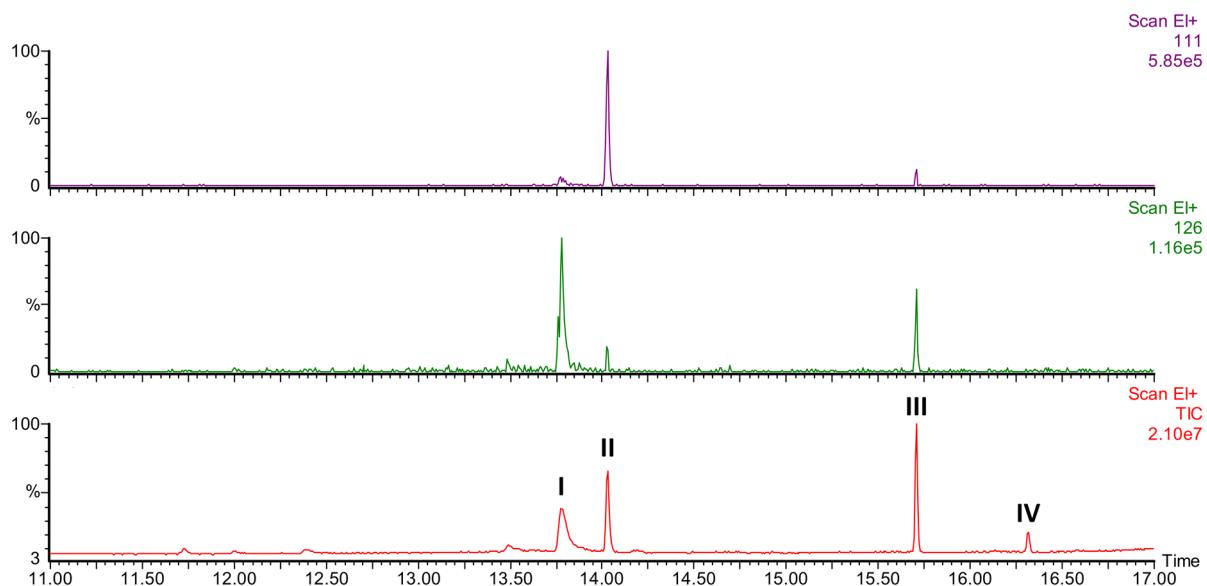
**Figure S21.** Accumulations of cyclooctanol in the course of cyclooctane (0.2 M) oxidation with  $\text{H}_2\text{O}_2$  (1 M) in the presence of nitric acid promoter (5 mM), catalysed by **1** or **2** (0.2 mM) in acetonitrile at 50 °C.



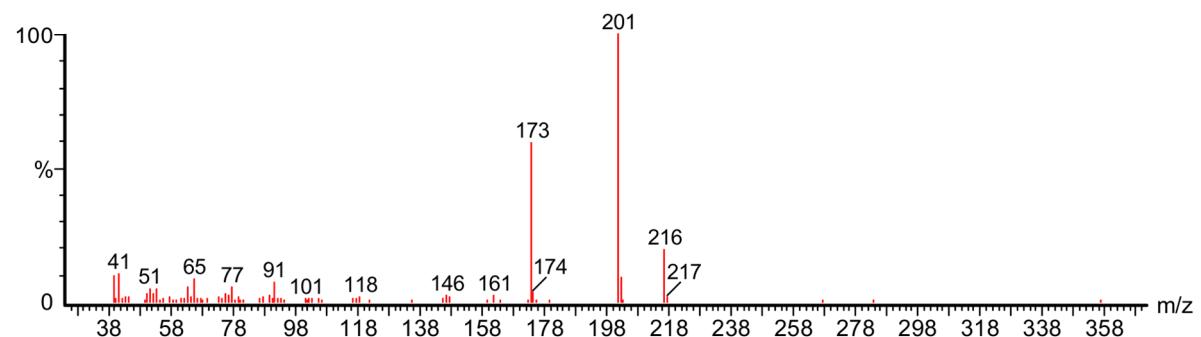
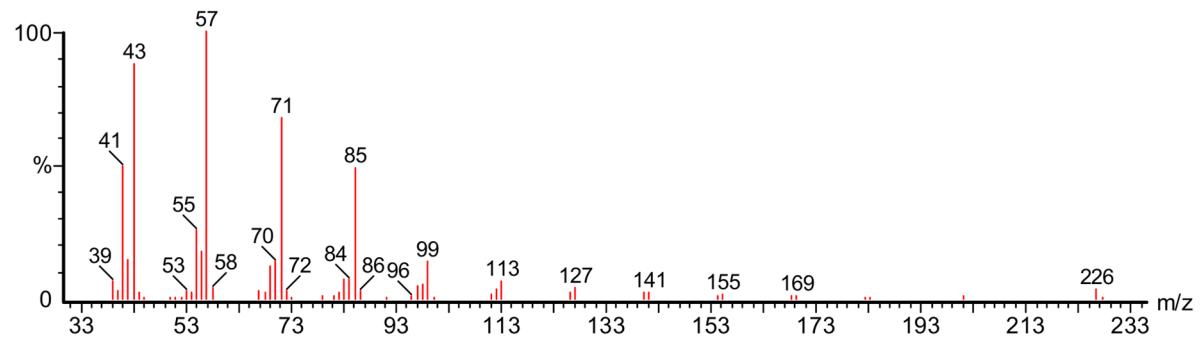
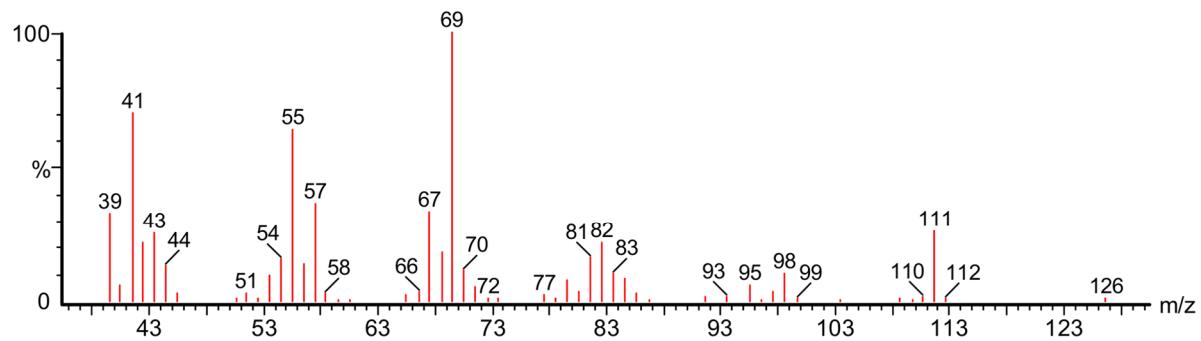
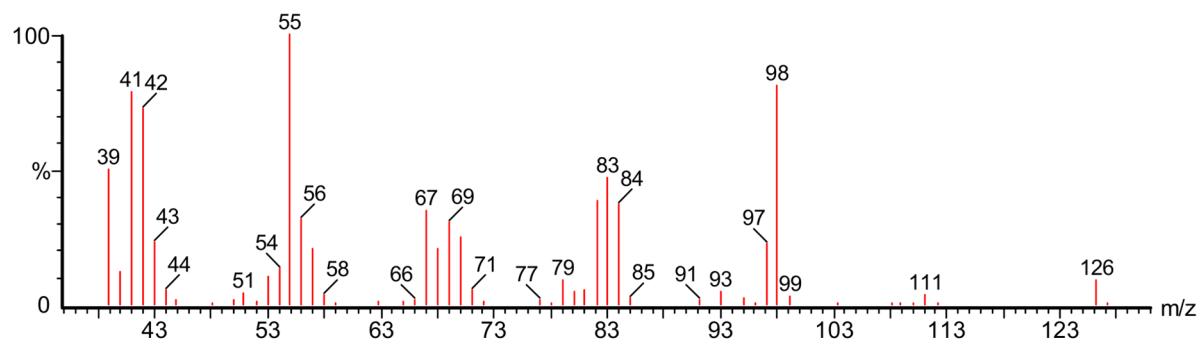
**Figure S22.** Fragments of the chromatograms (Phenomenex ZB-5 column) showing the main reaction products before (bottom) and after (top) addition of  $\text{PPh}_3$  in the course of cyclohexane (0.2 M) oxidation with  $\text{H}_2\text{O}_2$  (1 M) in the presence of nitric acid promoter (5 mM), catalysed by **1** (0.2 mM) in acetonitrile at 50 °C after 60 min. The inset shows the EI-MS spectrum of the peak 10.33 min, corresponding to cyclohexyl hydroperoxide.



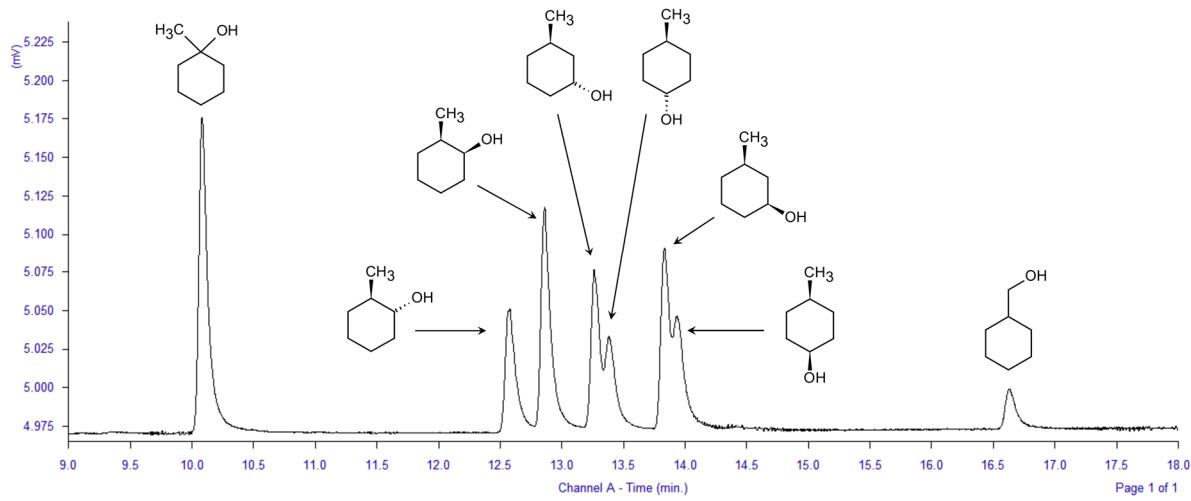
**Figure S23.** Fragments of the chromatograms (Phenomenex ZB-5 column) showing the main reaction products before (bottom) and after (top) addition of  $\text{PPh}_3$  in the course of cyclooctane (0.2 M) oxidation with  $\text{H}_2\text{O}_2$  (1 M) in the presence of nitric acid promoter (5 mM), catalysed by **1** (0.2 mM) in acetonitrile at 50 °C after 60 min. The EI-MS spectra of products **I–IV** are depicted in the Figure S25. The peak **II** was assigned to cyclooctyl hydroperoxide.



**Figure S24.** Fragments of the chromatograms (Phenomenex ZB-5 column; top: 111  $m/z$  signal, centre: 126  $m/z$  signal, bottom: total chromatogram) showing the main reaction products before addition of  $\text{PPh}_3$  in the course of cyclooctane (0.2 M) oxidation with  $\text{H}_2\text{O}_2$  (1 M) in the presence of nitric acid promoter (5 mM), catalysed by **1** (0.2 mM) in acetonitrile at 50 °C after 60 min. The EI-MS spectra of products **I–IV** are depicted in the Figure S25. The peak **II** was assigned to cyclooctyl hydroperoxide.



**Figure S25.** EI-MS spectra of the peaks I–IV (top down) depicted in the Figures S23 and S24.



**Figure S26.** Fragments of the chromatograms (SGE BP-20 column) showing the main reaction products after addition of PPh<sub>3</sub> in the course of methylcyclohexane (0.2 M) oxidation with H<sub>2</sub>O<sub>2</sub> (1 M) in the presence of nitric acid promoter (5 mM), catalysed by **1** (0.2 mM) in acetonitrile at 50 °C. The peaks were assigned on the basis of mass-spectra as well as earlier reports [26, 80].

**Listing S3.** Cartesian coordinates of the intermediates and transition states optimized at the B3LYP-D4/ma-def2-TZVP level in methanol (C-PCM model).

<u>General components</u>	<u>Reaction A</u>
<b><sup>3</sup>O<sub>2</sub></b> O -0.09751156225758 -0.09751156225758 -0.09751156225758 O 0.59751156225758 0.59751156225758 0.59751156225758	<b><sup>3</sup>I<sub>1a</sub></b> O 4.03845056419252 1.98157967770946 9.7676899836636 N 2.07030883426840 0.83954805927022 8.31051970807991 C 3.93049622016011 2.38120943645863 8.45931858626383 C 2.92400319907753 1.75752638756080 7.70236034865103 C 2.78092142803321 2.13154170743101 6.36518586356312 H 2.00861953717869 1.65454151400480 5.77221587097943 C 3.60667742506859 3.09589581983847 5.79518085215384 H 3.47310493019785 3.36602176787849 4.75505970360277 C 4.59821373390401 3.70404250690989 6.55597065815927 H 5.24687408626806 4.45381466404312 6.12155668834545 C 4.75617934712222 3.34010653222575 7.89235316960995 H 5.52523359451926 3.79988851411545 8.50375561532183 H 1.62306377610712 0.19359931563509 7.67609607126342 H 2.45890928726774 0.37050676292879 9.11576305464285 O 3.05070474965365 -0.61148936193150 11.57393138098391 O 3.47159857759727 0.16589745424503 12.39028955531188 H 4.76719070938357 2.44954924167640 10.19642287470077
<b><sup>1</sup>H<sub>2</sub>O<sub>2</sub></b> O -0.46887633102714 -0.13679053190581 0.12624007810060 O 0.45419970869139 0.96488365276615 0.29595808479288 H 1.05876063376623 0.61600079803069 0.97130154332497 H -0.14408401143047 -0.54409391889103 -0.69349970621846	<b><sup>3</sup>I<sub>2a</sub></b> O 4.15229259353445 1.95261296804817 9.78815249320881 N 2.23312289180532 0.64034349646986 8.23068600560421 C 3.96782321958931 2.29306050395033 8.57907687051217 C 2.97327134932211 1.62965218291615 7.72864677045460 C 2.81296371189585 2.04625644113641 6.38481470609727 H 2.07453807572018 1.54145626992137 5.77336628213578 C 3.57301555093279 3.06234540485098 5.87574161821205 H 3.44024728378620 3.37210830279954 4.84728124118061 C 4.53963784049764 3.71996945183888 6.68519244834586 H 5.12833921294198 4.52267859315442 6.25935007260127 C 4.72724979992642 3.34838980443998 7.98568017109222 H 5.45951400715283 3.83978688963756 8.61368593892353 H 1.54507895152037 0.18274406438580 7.65224764380797 H 2.31433567980494 0.32722257645482 9.19521694527874 O 2.37813914491415 -0.36002409077403 11.01765172286646 O 3.35177724826895 0.34227108224207 11.57149692748173 H 3.66797343838624 0.98601605852750 10.83110214219615
<b><sup>2</sup>OAP•</b> O 4.14166456200685 1.80261943151435 9.71113899749650 N 2.32896350455999 0.54589738429775 8.15006988169128 C 3.99244556020126 2.22429539821612 8.53583659328199 C 3.01679114619493 1.57503918153813 7.64467489983966 C 2.84019445101237 2.03799419408522 6.32657164696622 H 2.11648395196333 1.54511290195694 5.68799955406583 C 3.58086161102515 3.09909140841702 5.86634015201676 H 3.44168962404753 3.45054172753038 4.85183285240957 C 4.53062979114066 3.74593747084389 6.70216948893786 H 5.09778851288311 4.57988967070532 6.30730895934592 C 4.72970321438690 3.32776455165635 7.98750127166589 H 5.45027219301571 3.81312910596515 8.63441992861084 H 1.64255898693764 0.04611858857981 7.60867302251901 H 2.50534489062454 0.26564298469355 9.10336975115259	<b><sup>3</sup>TS<sub>1a</sub></b> O 1.02473197099497 -0.07877834973896 1.68490386646586 N -1.08474962075433 -1.41440743643944 0.34583539611055 C 0.63463407519315 0.28033439269890 0.47835991824378 C -0.41228470149822 -0.41590630386834 -0.23288186850444 C -0.73076397220069 -0.00454913423225 -1.55402755018803 H -1.51726074886953 -0.53301472051600 -2.07832690077603 C -0.05921320785705 1.02925626458337 -2.14333652841026 H -0.31162135189688 1.33350298460566 -3.15051043804849 C 0.9683895308013 1.70565368288800 -1.44386147619320 H 1.49558753119825 2.51994903410772 -1.92349419892645 C 1.29897941119060 1.33716242629548 -0.16094304593396 H 2.08048102646732 1.84664634385151 0.38740838621870 H -1.79120544256451 -1.90113542666299 -0.18747181423333 H -0.82716635419199 -1.82923369698806 1.24710963698942 O -0.60841383591407 -2.31610773817377 2.98223725683082 O -0.47485153129683 -1.08683122678584 3.39943092796110 H 0.31473279891965 -0.47254109562495 2.34956843239394
<b><sup>1</sup>BQMI</b> O 4.11646350293229 1.84160419361749 9.72993138113478 N 2.24342263495258 0.57638405010767 8.09436162942509 C 3.97485772534947 2.23499125894713 8.58035944120405 C 2.94857412275994 1.54983668762795 7.66656244192610 C 2.80313100397509 2.04056188034532 6.30209891496879 H 2.07647332567926 1.54778297082853 5.66866378812341 C 3.55317715874952 3.06586269514110 5.8671786288107 H 3.44971199370131 3.43363049830077 4.85440314631692 C 4.52514033826738 3.71551226906336 6.73322237629779 H 5.09618391129747 4.53764934401500 6.31813917243422 C 4.73306803555235 3.33630803817047 8.00991635527157 H 5.45878398370054 3.82786584540752 8.64516026021375 H 2.49018226308279 0.37966026842768 9.07050240980240	<b><sup>3</sup>TS<sub>2ab</sub></b> O 0.04139182131538 0.63503189464089 1.74078065432350 H 1.15017014537391 0.04237638347204 2.6259398144439 N -1.18394223186724 -1.49804375031184 0.62477259275430 C -0.02686585551579 0.58817652246689 0.47284723642265 C -0.68986460583081 -0.55074267286009 -0.17126886595815 C -0.78627700040584 -0.61340389264823 -1.57924325511630 H -1.27984844566014 -1.46342027613463 -2.03435792326276 C -0.25795930870405 0.39230687756588 -2.34287761301285

H -0.33127671379912 0.34389808209584 -3.42163398452990  
C 0.38983945609786 1.50581527373527 -1.73912722045861  
H 0.79790325233506 2.28337869322443 -2.37252670338062  
C 0.50095199579411 1.60154278637657 -0.37962312768862  
H 0.99180341150465 2.44471668820258 0.08974458296680  
H -1.65162782846143 -2.31189708776690 0.25739709730467  
H -1.08259181454288 -1.40258797218252 1.62495495607024  
O 1.54711649937647 -1.63478079844781 3.37871047351644  
O 1.87107722298989 -0.36236675142836 3.22551121860480

### Reaction B

<sup>3</sup>I<sub>1b</sub>  
O 3.81637064742863 1.69295763714747 9.80438733444807  
H 4.48123568561814 2.14922196155590 10.33681794643728  
N 2.05177101792253 0.59045710609626 8.08153727991633  
C 3.80945166124400 2.19409423294886 8.52626080288932  
C 2.91127891198118 1.59016592614265 7.62991198705175  
C 2.87441025158128 2.06431932248056 6.31763699694885  
H 2.18655926938033 1.60280555843969 5.61792677412540  
C 3.69947359531651 3.10638052439426 5.90498227174563  
H 3.6508657572778 3.452771120931323 4.88010276739234  
C 4.58132611139699 3.69544971252893 6.80340440730019  
H 5.22753359494803 4.50636001735837 6.49284879360071  
C 4.63230996262771 3.23259460978439 8.11705523754108  
H 5.31371772051682 3.67820390615058 8.83354624147854  
H 1.70214276692597 -0.02263927733453 7.35923780850628  
H 2.38748988438511 0.07589516737900 8.88303383573683  
O 5.84390507387247 3.51875435022721 12.11140590462289  
O 6.64151808732616 4.28802803538696 11.64172361025782

<sup>3</sup>I<sub>2b</sub>  
O 4.10486866097951 1.85257316818539 9.80384101021873  
H 4.96736709463740 2.50379054558531 10.86142860159800  
N 2.46445113173726 0.48435848067497 8.17899928139968  
C 3.96369453398937 2.29366165332853 8.62019902125519  
C 3.07535259927807 1.57078006692952 7.70599337619056  
C 2.89376557804867 2.03055862491283 6.38312517509676  
H 2.23299931276283 1.48123156389877 5.72386866634178  
C 3.54932353351747 3.15427227877804 5.95654815525736  
H 3.40983329616800 3.50642188379256 4.94278320497538  
C 4.41559388487078 3.86993382028128 6.828999298879265  
H 4.91908593250821 4.75444382469770 6.45985812241751  
C 4.61706551830127 3.45711027916091 8.11667915717231  
H 5.27499924151953 3.99309715360777 8.78869890739046  
H 1.84124396702897 -0.06519516976018 7.60853824536106  
H 2.63156296407300 0.20109355685464 9.13346415922827  
O 5.52040979317330 2.88073187061259 11.65310496053848  
O 6.21696295740609 3.89723639845922 11.17049696676542

<sup>3</sup>T<sub>S1b</sub>  
O 0.02378386812047 -0.33656317302349 1.78373321708345  
H 0.92996062317082 -0.08699101017694 2.31355021856334  
N -1.54486331245492 -1.78220943814480 0.16446816613959  
C 0.01997065016255 -0.00884670812902 0.51242552468549  
C -0.83456336282584 -0.77843369196710 -0.35860799663401  
C -0.90046664845663 -0.44674167300374 -1.73218318845823  
H -1.5461113221856 -1.02894260133330 -2.37758410343662  
C -0.14766959842285 0.58620609779880 -2.22336981910674  
H -0.19503344869341 0.83409910865138 -3.27564483113999  
C 0.69843665035500 1.33466732371054 -1.36938303396741  
H 1.28644544745895 2.14513384019998 -1.77981148125603  
C 0.77498672586743 1.04537774225218 -0.02645446552240  
H 1.41300548818503 1.61885295710371 0.63297008106721  
H -2.15118658372762 -2.34865845827530 -0.40792309199911  
H -1.47045524077582 -1.99735585364212 1.14721365984983  
O 2.04084106367713 0.18252027037902 3.07559908578009  
O 1.60291881057826 1.06788526760024 3.92100205835153

### Reaction C

<sup>3</sup>I<sub>1c</sub>  
O 4.40151318284024 1.42038291216173 9.39835120290343  
N 2.35609907005673 0.43881307765906 7.86951459100458  
C 4.10515907630216 2.02300862029396 8.33200270444395  
C 3.01180437083281 1.53344995873333 7.48004254503521  
C 2.68532091066053 2.21871065716030 6.28883291578617  
H 1.87486782572228 1.84105110674847 5.67620525325077  
C 3.38448392538027 3.33898621898573 5.92045667737433  
H 3.12637639633968 3.85730579539062 5.00582870509229  
C 4.44787221868110 3.83121751423159 6.72504941548921  
H 4.98272082234357 4.71788383278460 6.40790905996883  
C 4.79460510337144 3.19850687033132 7.88511269404758  
H 5.60243049187142 3.56360236995032 8.50739960191910  
H 1.60066375678403 0.07274573126655 7.31144356318792  
H 2.5917174235382 -0.05277678022033 8.72859065763975  
C 3.52890853586741 -1.33492121986046 12.10956074641307  
C 2.59161878702844 -1.95281214266381 11.16051727962858  
C 3.71617098160789 -1.90565051428217 13.38785494898323  
C 3.02787506649732 -3.03476474819107 13.74966947790672  
H 4.41195176473437 -1.43423304501648 14.07219644915499  
C 2.11566326472634 -3.65121110694615 12.85065836862302  
H 3.17842503253332 -3.4649400222030 14.73155360218559  
C 1.90663944332112 -3.13188315675018 11.60452704681183  
H 1.58558742466037 -4.54180920908077 13.16484109524062  
H 1.21426662499554 -3.59179964516991 10.91009569204230  
N 4.17814345446387 -0.23580133160473 11.72166864717062  
H 4.84135499748967 0.20777641561219 12.33770562310147  
H 4.05928911947447 0.15794907043953 10.79088590845009  
O 0.41796660905953 -1.44991722974297 10.01823552714405

<sup>3-1</sup>MEPC<sub>1c</sub>  
O 5.24729935525788 0.44572470091596 8.47371009831636  
N 2.52069781704153 0.11264930092236 8.22129653050059  
C 4.55481770590239 1.40419531210310 8.03342765740502  
C 3.09867676622548 1.26031768301443 7.85972930877208  
C 2.35044786849887 2.32425148860451 7.30549442640093  
H 1.28319486734233 2.19341724453131 7.17047510428661  
C 2.96332259012286 3.50013575876673 6.96226517010691  
H 2.37664875022426 4.31260155132733 6.55294075133795  
C 4.36404874794574 3.67114777166122 7.13785927977608  
H 4.82041755534765 4.61249686085317 6.85798847134846  
C 5.12839913405742 2.66182042225464 7.64803423786803  
H 6.19768512550305 2.77392635199513 7.77897255024665  
H 1.53746591450328 -0.03666326129491 8.05786481005812  
H 3.06387474044862 -0.65692599193423 8.60804804136168  
C 3.50438175483864 -1.07474084588621 11.62906165858546  
C 3.20589845313376 -2.21227053375402 10.74089987926870  
C 3.0580072200284 -1.09691555064868 12.97003846810592  
C 2.32867201573306 -2.15596600697946 13.44271883405707  
H 3.29653633680055 -0.25662004388470 13.61132030835468  
C 2.01805878417363 -3.26069197143027 12.60294988845519  
H 1.98201741123022 -2.15506005193408 14.46820841560636  
C 2.44463241439702 -3.28936326842867 11.30690602577988  
H 1.44033802555365 -4.08396101391279 13.00477354205742  
H 2.22248387928573 -4.12719996968585 10.65744639272384  
N 4.20803015039849 -0.04940575867026 11.14192092590126  
H 4.49347774058076 0.70400324095479 11.74768025210523  
H 4.57060544569517 -0.06032130441300 10.19018761495075  
O 3.63397337775461 -2.23168211504760 9.55469135626120

<sup>1</sup>TS<sub>1c</sub>  
O 1.50730015780854 0.13379778700398 -1.00433420390286  
N -0.83501373477363 -0.08406614374819 -2.43239665542926  
C 1.03025796011305 1.20800823714030 -1.59589664090403  
C -0.20305245918870 1.13200454076323 -2.32637332654715  
C -0.69539929596832 2.27729716812275 -2.96431660991296  
H -1.62647128222338 2.20842998105129 -3.51623448041522  
C -0.0088708519707 3.48037831321613 -2.89931496118775  
H -0.40998191896631 4.35351460909728 -3.39910261529775

C 1.19389904829160 3.56861586494921 -2.18896121663705  
H 1.72888987114689 4.50904603063658 -2.13994783084261  
C 1.69465818896386 2.44912363516405 -1.54542924409109  
H 2.62284963599418 2.49797062163269 -0.98760132433849  
H -1.80782274830129 -0.07124426082304 -2.69696216747433  
H -0.59719377306516 -0.77847935709762 -1.73636053355162  
C -0.04882297128850 -1.10007749843508 1.81817513903791  
C -0.49174078080033 -2.31465967394707 1.03252025998945  
C -0.02271122087181 -1.16215347708596 3.25083653086829  
C -0.36853726889523 -2.30488725416188 3.88561960835940  
H 0.28072813462535 -0.27787236306228 3.79785534605698  
C -0.74801816032881 -3.49050451292837 3.15124153513404  
H -0.35384842079320 -2.35053369676222 4.96679930362220  
C -0.79261345860240 -3.50769885001925 1.80128104017048  
H -1.00235446354754 -4.38015444824219 3.71389924807482  
H -1.08344146665803 -4.39028624139328 1.24666635783655  
N 0.28778382550486 -0.03493481956126 1.15116789678786  
H 0.61143840738367 0.74899956083023 1.71129544248894  
H 0.73096453535665 -0.05663380448965 0.09719496817462  
O -0.59286925571895 -2.26299994785038 -0.19132086606937

<sup>1</sup>I<sub>2c</sub>

O 5.12717098738533 0.38758478454475 8.59659553135993  
N 2.42976315514113 0.10799268640271 7.86267981756324  
C 4.44571247616538 1.45120761871223 8.05236756074684  
C 3.08483992960212 1.32117245023961 7.70784717461057  
C 2.43952651736932 2.42584320603870 7.14034642993597  
H 1.39096088241211 2.33727180593672 6.87782024141631  
C 3.12250187450498 3.61068305546041 6.89255264007304  
H 2.59640155508097 4.44642119593154 6.44728697158732  
C 4.47223095755602 3.7203688002623 7.21028321828559  
H 5.01275007133636 4.63825483215437 7.01703518867191  
C 5.12178297631533 2.63572290860894 7.79567321370450  
H 6.16867558125825 2.69676574219026 8.06867770078276  
H 1.42438929353475 0.16120340081706 7.92409167867098  
H 2.82916564308416 -0.55550367376102 8.51277309936802  
C 3.35493839536842 -1.06157776589059 11.63765122965440  
C 3.07304191688619 -2.30811313486722 10.79234470220254  
C 2.97361490266641 -1.08325037444977 13.04404390775828  
C 2.46729677144911 -2.19914314430908 13.59194067905199  
H 3.13464558491516 -0.18231941464708 13.62403470383054  
C 2.26788800948264 -3.40832523335966 12.80737973694897  
H 2.20048467409691 -2.22302489678284 14.64074349879864  
C 2.55720517033754 -3.47377393910335 11.49397114249856  
H 1.86317875746780 -4.27614847614010 13.31406341028076  
H 2.39369169208082 -4.37129914542954 10.91179179217187  
N 3.93259752905781 -0.08173846564121 11.05851654499215  
H 4.08123869927534 0.70402005837326 11.69379080355577  
H 4.68026860594182 0.10174736853868 9.43479547098592  
O 3.26814739022753 -2.29314224959411 9.5858191049180

**Reaction D**

<sup>4</sup>R<sub>1d</sub>

[Cu<sup>II</sup>(HMeEa)(OAc)(MeOH)]<sup>+</sup> + <sup>1</sup>OAPH + <sup>3</sup>O<sub>2</sub>, the latter are omitted

Cu 9.08401963440412 6.58858330031394 6.02020034859552  
O 7.16350601089946 6.87153749056112 6.41425549609691  
N 8.88488322894898 4.95193313941594 7.20268622737375  
H 9.34536215852113 5.23655804467048 8.06662800621331  
C 7.43360114041036 4.79708711147543 7.48378758966919  
C 6.80764518282379 6.16620089000587 7.61870667801504  
C 9.50705666485589 3.69389061205706 6.74180921140566  
H 7.27742685584499 4.19938681406125 8.38418404732613  
H 6.99099294326401 4.27310226145952 6.63588122478119  
H 5.72218180148991 6.09572543880537 7.69326530228634  
H 7.19704963729530 6.69932232836526 8.48950000721917  
O 9.29030063558837 8.31651074058003 5.17470286667118  
C 8.57704044158484 9.35485825332720 5.42946169792729  
O 7.54286822673401 9.35094531150562 6.13062422462012  
C 9.08139169849767 10.64725141841101 4.83836806566855  
H 9.08220716062253 3.41880666115881 5.77806686248661

H 9.32111696244422 2.89175220215052 7.45971011855431  
H 10.57848522862848 3.83882526486325 6.63318407320875  
H 9.91238545970908 11.00454213688170 5.45229804357175  
H 8.29825042095140 11.40209341846336 4.83374859658687  
H 9.46084189803657 10.48433850721891 3.83025762498109  
H 7.12880592933809 7.88807336270822 6.46903014011698  
O 10.9819327747710 6.16847910974309 5.44440976782634  
C 12.08036335326611 6.50741238984741 6.32845434523017  
H 11.90074975749909 5.98586660049076 7.26506570822627  
H 12.11350226480027 7.58310122597776 6.49932090556153  
H 13.01197842260685 6.16187132886224 5.88338149827458  
H 11.12983660345722 6.59616663661870 4.58791832150526

<sup>4</sup>R<sub>2d</sub>

[Cu<sup>II</sup>(HMeEa)(OAc)(MeOH)]<sup>+</sup> + <sup>3</sup>O<sub>2</sub>, the latter is omitted

Cu 9.07484639168600 7.34164556018023 6.67430492276568  
O 7.34192138342789 6.55197010209751 5.93886111758196  
N 9.20331084817507 5.53336668924840 7.63684588791228  
H 9.08217637078965 5.78646863484352 8.61647870209865  
C 8.03641188095091 4.71260010300939 7.21803493724261  
C 6.86049762767473 5.60835193913015 6.90797121298724  
C 10.46431054650397 4.77663470126268 7.49784084353288  
H 7.78410013403954 3.98161268373478 7.98962192091870  
H 8.32401612384787 4.17366364787977 6.31481239266729  
H 6.03574419148480 5.02917814538329 6.48884852625909  
H 6.51060607546768 6.13325922538577 7.80130880774429  
O 8.67312136020692 9.11285856236409 5.89524262702460  
C 7.52341426213002 9.56103285846259 5.55536389035594  
O 6.45586918655770 8.91133433434492 5.62041013695240  
C 7.5080445736865 10.97315754611064 5.01859037777510  
H 10.61155423046778 4.52842582033329 6.44914334169576  
H 10.42543734063310 3.85482475287647 8.08361497906297  
H 11.29924451373586 5.37928542795057 7.84181647048850  
H 8.10833995496431 11.62617312371815 5.65211395255819  
H 6.49034525532904 11.3499309319746 4.94478953544786  
H 7.96052722166526 10.97177726394648 4.02383935095857  
H 6.78574235202969 7.39469403766019 5.86367722010159  
O 10.21930724653304 6.65243304148082 4.78884438458012  
C 11.59207339675758 7.02224727625779 4.58351136716737  
H 12.16792921374352 6.55239648464151 5.37750087880596  
H 11.71934644489556 8.1056557712860 4.63877893038219  
H 11.94680543062770 6.65913421897055 3.61762546170972  
H 9.69525922942451 6.97581807904737 4.04469436607061  
C 11.09978111207966 7.22581781960636 9.85249820754078  
C 12.74621561619903 7.77728679867263 8.18372456046487  
C 13.72454360101385 7.13696786548211 8.93388846313265  
C 12.07719391928617 6.59202014301866 10.60810119769503  
C 13.38806906074631 6.54631102692461 10.14761790842354  
H 11.80278003190548 6.13114015491094 11.54985730758875  
H 14.14374564423101 6.04722653129067 10.74041622528677  
H 14.74413190867694 7.10508455848708 8.57325703682081  
O 9.78302583440612 7.27983156546258 10.21686482385627  
C 11.43363302790308 7.82453978949161 8.63526821437820  
H 12.99430011318148 8.24448679788029 7.23870557663820  
N 10.40378973848643 8.42867106476466 7.85720298622523  
H 10.78520221213814 9.09665945196229 7.19382138716647  
H 9.74260536340552 8.92699052658845 8.44871175800379  
H 9.65876814522214 6.89736777480979 11.09706680393029

<sup>4</sup>I<sub>1d</sub>

Cu 9.05124331761630 7.29017826620448 6.65748129628932  
O 7.34898300031107 6.45089930181380 5.91502001406146  
N 9.23321092004215 5.48456849522148 7.61483632588317  
H 9.10551357058269 5.73042833365255 8.59541995766534  
C 8.09089738856526 4.63040461485954 7.19342890543289  
C 6.89014323313656 5.49138036263169 6.87990426985197  
C 10.51541374545074 4.76541607219429 7.4711579409840  
H 7.85842476930758 3.89195715487111 7.96409394870220  
H 8.39644789136760 4.10028887585706 6.29090732671847  
H 6.08500037243799 4.88934304247592 6.45501825920884  
H 6.52041696197096 6.00397450929812 7.77236506416257

O 8.59829679983776 9.05452338133904 5.88857252509737  
C 7.43923340244994 9.46515218085418 5.53369067420481  
O 6.39285098637299 8.78043797749627 5.58309165777350  
C 7.38421712108135 10.87661156719453 4.99781247159122  
H 10.66809181127719 4.52563084125122 6.4212433533664  
H 10.50449671487593 3.84032023962778 8.05296033544197  
H 11.33342460037302 5.39018992739297 7.81584512233408  
H 7.96855482980754 11.54615419613671 5.62882897347334  
H 6.35643484026089 11.22554579717596 4.92616086463975  
H 7.83311055800014 10.88669290544556 4.00137188537933  
H 6.76648264154984 7.27527847955740 5.83326621248903  
O 10.22343424305827 6.64869330405927 4.76489237055677  
C 11.58715520822390 7.05274665053702 4.56696510854817  
H 12.17478103622954 6.57730263794788 5.34900036238600  
H 11.69169415943597 8.13710948814609 4.64748771164894  
H 11.94891854719701 6.72037845594798 3.59259607802622  
H 9.69256805014667 6.97218036412880 4.02567081020138  
C 11.06990200813256 7.22394231280428 9.83230520591898  
C 12.71773742977381 7.80180989820740 8.17380975098496  
C 13.70201271885669 7.17913526295917 8.93097918039340  
C 12.05293064881521 6.60633618855057 10.59427768422737  
C 13.36734360339128 6.58307697322083 10.14265169353559  
H 11.77940679045046 6.13854226486345 11.53217140488126  
H 14.12712439829516 6.09630414591867 10.74043858653569  
H 14.72436177642897 7.16458549898215 8.57713248800768  
O 9.74985546573379 7.25504715222418 10.18683464207447  
C 11.40120166128151 7.82580850256310 8.61583274986512  
H 12.96418466979153 8.27188535135939 7.22979563435014  
N 10.36498215691888 8.40882057200372 7.83004259896303  
H 10.73792066960102 9.07831515776762 7.16335171191480  
H 9.69558896406309 8.90188623385832 8.41677315857004  
H 9.62661777006393 6.88728234184051 11.07322427550455  
O 10.74324117984174 6.05492870458289 14.24790864506920  
O 9.59916736758482 5.84738565496863 13.93655014300325

<sup>4</sup>I<sub>2d</sub>  
Cu 9.09306286181176 6.61644049619848 6.08001849091561  
O 7.14080383679422 6.86630827337036 6.34494675805637  
N 8.85314075713803 5.03654864513818 7.31873410322816  
H 9.16881725663571 5.42510359025802 8.21332527550864  
C 7.39576023088507 4.77479195496204 7.40361738925049  
C 6.65299535317459 6.09004035376833 7.45510624527268  
C 9.62454856877245 3.80975592557148 7.04721336182247  
H 7.16513230041582 4.16324457527003 8.27918396037933  
H 7.10827268209229 4.22088398713570 6.50883000905913  
H 5.57931961970832 5.93477235157531 7.34535571426414  
H 6.83937636965575 6.61968969439958 8.3909739341405  
O 9.33013114717754 8.3549615828296 5.26774512382921  
C 8.61094747502926 9.38685879517448 5.52912663902814  
O 7.55599650064803 9.36572885779147 6.19939210002907  
C 9.13855770825301 10.69598071105501 4.99950219700933  
H 9.37909829007283 3.44208510061117 6.05256572424801  
H 9.38517730137361 3.04022634779914 7.78494972235423  
H 10.68708602617824 4.03051846943579 7.09686615982230  
H 9.93315850246648 11.03821671616240 5.66798129497172  
H 8.35299288333429 11.44798323326829 4.97521246423341  
H 9.57210766499548 10.56328065120764 4.00914205580036  
H 7.08858650381456 7.87265725308206 6.45093870306233  
O 10.90314735647474 6.07904491864941 5.32148366526327  
C 12.12912740053710 6.40872608994514 6.02170474885992  
H 12.10439565661248 5.87900750668494 6.96824655134450  
H 12.19113100296783 7.48173282185003 6.19525302984991  
H 12.97622470839986 6.06774975622389 5.42881232757553  
H 10.94668611179510 6.46188223483660 4.43271748335293  
C 10.95745289684350 7.22660699005271 9.44541855419250  
C 11.30568886338679 9.49527584896909 8.47057408396001  
C 12.65730713289693 9.30933140585651 8.56713690484263  
C 12.37120445813663 7.10400087578959 9.54492694278861  
C 13.19144041165118 8.11165349195377 9.11786930261131  
H 12.77646772071102 6.18560459633470 9.94916980752487  
H 14.26582679567434 7.99920952540752 9.18823048413610

H 13.33349396962539 10.08266244681687 8.22694702255450  
O 10.13416117810891 6.30882500502661 9.77139089458021  
C 10.42628115750614 8.48687810138947 8.92324417247834  
H 10.88982597543049 10.40803436010351 8.06255500451760  
N 9.10300283243906 8.62242724330177 8.89565940863914  
H 8.65200994311687 9.43760304180497 8.51020557290023  
H 8.52907322503904 7.87909088505938 9.26358918632951  
H 10.58284804375714 4.94746622107260 10.30674067646905  
O 11.18844194775844 4.23181945275868 11.94102265078989  
O 10.81271137068978 4.01816961410613 10.68958063887009

#### <sup>4</sup>T<sub>S1d</sub>

Cu 9.05148470327354 7.14659986616426 6.65554757935860  
O 7.25176165250069 6.49218368544013 5.89724412783166  
N 9.11892214685044 5.28765324794595 7.47786790286508  
H 9.00809672644234 5.47138815077031 8.47664944169357  
C 7.92837793417366 4.53443452816262 7.00210123562876  
C 6.77033323104233 5.48303027616451 6.80108812715629  
C 10.36016781404260 4.51104905390164 7.29208586675588  
H 7.67286477725621 3.74068240613673 7.70763273037893  
H 8.18963933600325 4.0770605058847 6.04704664580252  
H 5.91832677084922 4.96295419581018 6.36006441666038  
H 6.46091094085984 5.94155333565475 7.74420853715193  
O 8.77879030550338 8.96465749090414 5.99088194100168  
C 7.64145529585502 9.52103341560678 5.77826463849774  
O 6.53815556010198 8.94496069373965 5.87759669859114  
C 7.70335022310804 10.97231647244417 5.36639348308757  
H 10.50044050102812 4.31416950530883 6.23204426671930  
H 10.30318778269108 3.56338971548915 7.83275710098542  
H 11.21285892064988 5.07659636832448 7.65866807555623  
H 8.30583326215834 11.5362128018367 6.07966920396013  
H 6.70574136150904 11.39994393816227 5.29934984644123  
H 8.19495515309840 11.04387356591173 4.39369557783347  
H 6.74592193395118 7.36328879604514 5.94231075069389  
O 10.38088825386457 6.65124989009287 4.93635775696218  
C 11.77183547075188 7.02155015884175 4.95036088561183  
H 12.22300455721129 6.52265544139483 5.80402232155439  
H 11.88614620720305 8.10137807243167 5.05966273913058  
H 12.25991476819501 6.68725844032144 4.03409617221901  
H 9.96666276892838 7.03131001949171 4.15024120615272  
C 11.11854048461725 6.60894992250899 9.86097653944647  
C 12.47198501002146 8.03982554354632 8.40451034913178  
C 13.61665871613675 7.46473305460354 8.93700209003856  
C 12.31653501659552 6.04866218626795 10.38788668587056  
C 13.53714589215333 6.46740212196847 9.93100876210407  
H 12.22113933729829 5.28369430942557 11.14737311655252  
H 14.44656660734398 6.03692955771298 10.32886161680195  
H 14.58682465627837 7.79077400187157 8.58541327393253  
O 9.94957596032655 6.19701644321466 10.23008519054641  
C 11.22540205734868 7.63425614170286 8.85165574162264  
H 12.54371049429932 8.80581230756147 7.64309116737293  
N 10.04348359471448 8.15157549289624 8.31593541543818  
H 10.15216954791500 9.07356393555050 7.90558374845421  
H 9.27780847652607 8.15183534561728 8.98461704394251  
H 9.57997570675070 6.89237430919784 11.28277799703443  
O 10.60227078221455 8.36620888191321 11.92274193697695  
O 9.54319930034754 7.65018685499987 12.09574004844448

#### Reaction E

<sup>3</sup>R<sub>1e</sub>  
[Cu<sup>II</sup>(HMeEt)(OAc)<sub>2</sub>] + OAPH, the latter is omitted  
Cu 8.80285620298044 7.73527965564826 6.52068944949056  
O 6.87846379928537 7.41446098786902 8.03653774977323  
N 9.17002593954951 5.86407230502047 7.20637805702439  
H 9.74642953289369 5.96109833092219 8.03975272580548  
C 7.88083042975595 5.25364507347237 7.59822402391461  
C 7.14523171397340 6.12296416324019 8.59845977445965  
C 9.90467668347081 5.03686573350431 6.22872856824020  
H 8.04654435876036 4.26021383947931 8.02819632004330  
H 7.28331282313608 5.13494673804050 6.69230787974134

H 6.19979118204816 5.64273297519947 8.85960805290705	O 8.00313023535182 7.25374420579292 4.85943398351091
H 7.73597079727911 6.22975085715942 9.51251846887395	C 7.44462703333452 8.84694690120251 3.13896873768122
O 8.35050633543358 9.37085803855281 5.38048354548871	H 9.41472476820515 5.02881645816100 5.68427185636816
C 7.96148280354354 8.60282391762320 4.44420548626953	H 9.95441256064070 4.14591093499595 7.13024302977950
O 8.04297334110921 7.34904014784799 4.61491577387786	H 10.81120848670925 5.61410302844616 6.60825111475884
C 7.39062776452639 9.16939509873990 3.18092632811815	H 8.04532711701858 9.65183734013293 2.71633961488593
H 9.3295583869852 4.97885222461258 5.30658135605441	H 6.42161577530494 9.21653939474549 3.24805605592546
H 10.06413013592153 4.02689177510834 6.61580479210550	H 7.43716811220546 7.98813159630037 2.47102269547907
H 10.86806087244479 5.49843107610665 6.01932241674045	H 7.03636898849816 8.15478201746701 8.57262417681767
H 7.75950757769757 10.17840613105717 3.00714124658649	O 8.43800006911328 9.02825114311317 9.20737044826881
H 6.30302470811312 9.21202235412454 3.28488895150764	O 9.43064656697555 8.83689844624994 8.16109266691502
H 7.62387426334431 8.52551686142363 2.33428973542414	H 12.84324999310648 5.68952046632218 9.11897225888119
H 7.34027643368930 8.08816375905481 8.57670661787856	C 11.97281950187734 5.53390890099109 9.74373436227063
O 8.86903742692652 9.01017841766980 9.00000046115806	C 11.69067025699392 4.22619194562504 10.22321581709589
O 9.67632903541841 8.66742953852278 8.03867766851652	H 12.34993231010492 3.41076332456575 9.95527233427890
<b><sup>3</sup>I<sub>1e</sub></b>	
Cu 8.70108463922760 7.65537800328182 6.68521852813034	C 11.15817588502281 6.58622785811999 10.05690703061315
O 6.74391359144181 7.31179880775842 8.10745018530160	H 11.35054814180941 7.58394023532969 9.68582271894046
N 9.11734314955681 5.82059908761522 7.4369440741710	C 10.598870159630138 3.98531375250095 11.01629610672661
H 9.67901055650386 5.9615824779515 8.27493578090043	C 10.00010608954001 6.40233667166290 10.87616095179379
C 7.84414703960984 5.17184958002609 7.81725894813599	C 9.73607476583205 5.0445762958224 11.36635045089420
C 7.02030175422891 6.05203619007869 8.73631526853550	H 10.38260533016065 2.98873187443331 11.38165000361506
C 9.90547294224301 4.99007695515961 6.50608457282738	O 9.19483659045084 7.33214667739685 11.17097357925416
H 8.04127683581356 4.21463273077708 8.31044008528048	H 8.39906670926222 3.97454607784566 12.49914667322736
H 7.29096319769573 4.97168808325627 6.89750292534352	N 8.65391406355444 4.87571612376174 12.12745393326208
H 6.07723117623584 5.54770268875164 8.95698205633065	H 8.07394128592464 5.67569374744068 12.33455087211448
H 7.54347120530468 6.21718905719298 9.67903229135842	H 8.79096041775198 8.46958160163364 9.94490882465430
<b><sup>3</sup>T<sub>1e</sub></b>	
Cu -0.25111995602592 1.25620265835407 -1.37964288270610	
O -2.30869397330608 0.92312954187993 -0.08886888904304	
N 0.04212005753937 -0.63214900028037 -0.69353019160689	
H 0.50363916143186 -0.53637977417772 0.20837592104699	
C -1.28623833402009 -1.24743376297743 -0.49479731828300	
C -2.15858740998864 -0.40785644352044 0.42122834703334	
C 0.90878427131028 -1.43882546323748 -1.57243555181465	
H -1.18020343688167 -2.25223050547815 -0.07170339071087	
H -1.75256726323510 -1.34165127166489 -1.47711723759982	
H -3.14388330620679 -0.87395763170890 0.48808169222110	
H -1.73445645185567 -0.37478991533645 1.42646216392772	
O -0.64348561603112 2.87809323493845 -2.60838831210440	
C -0.98192228828558 2.06381151088749 -3.52071094027225	
O -0.90652237556153 0.81839967041971 -3.27827347364171	
C -1.48591390255176 2.55244955326738 -4.84326545282834	
H 0.46297346659325 -1.49226575431432 -2.56410841592297	
H 1.02736484214154 -2.45071697943138 -1.17637609897170	
H 1.88634741495474 -0.96625445960229 -1.64437595942948	
H -1.16541093609846 3.57598564923710 -5.02641737880009	
H -2.57872966279529 2.52623399648925 -4.82660134688797	
H -1.14692234417029 1.89684270157717 -5.64446052239155	
H -1.86482549883628 1.54410547473357 0.52670261439911	
O -0.41830387055488 2.47582480622445 1.11503177847201	
O 0.51286069752574 2.17318901838270 0.14749663428396	
H 3.88690029391314 -0.68902339786660 0.83199093081453	
C 2.98201182608909 -0.76980608687134 1.41982034893328	
C 2.47527753917013 -2.03288822377935 1.7603453277823	
H 2.99197617916624 -2.92559490747197 1.43087831719836	
C 2.31981127573794 0.36901922658303 1.83457846542367	
H 2.68813632364000 1.35428342679884 1.58431257971371	
C 1.32306571302602 -2.15639894924895 2.51491085762466	
C 1.13761006784224 0.28269241532344 2.59780996945438	
C 0.63503824927637 -1.01527450277523 2.95364823742473	
H 0.93570174044430 -3.13473497786739 2.77317299368438	
O 0.47289158946359 1.34396873897524 3.00663921902892	
H -0.83350767918553 -1.96581323981423 4.03901211382697	
N -0.51041252039030 -1.08638669715394 3.67260653984347	
H -0.90007955408498 -0.23848905065543 4.05023528695372	
H 0.05927567080010 1.99468937116246 2.10773297892758	
<b><sup>3</sup>I<sub>2e</sub></b>	
Cu 8.69257153382446 7.83381691667474 6.71047878148729	
O 6.52638463236637 7.51281873888590 8.03061879329568	
N 8.94215973200448 5.97768900603360 7.49860638503795	
H 9.3864069118797 6.12298417562980 8.40166959300501	
C 7.61909620607724 5.35587251556203 7.70490460166922	
C 6.72819188534406 6.21120730039238 8.58821987734433	
C 9.83599063817743 5.13634187466270 6.68231324353787	
H 7.73385362488135 4.36598358175206 8.16048510040005	
H 7.16128523317316 5.22464395210048 6.72280777489352	
H 5.75918257803193 5.71694926468335 8.68530033408723	
H 7.16145823736249 6.29781875158880 9.58839461754104	
O 8.34026256228046 9.36266232915113 5.31141760858947	
C 7.96040501093512 8.47084457606297 4.49551299109739	
<b><sup>3</sup>I<sub>ea</sub></b>	
Cu 8.75968363661136 7.74020452023083 6.54546130341056	
O 6.87559123855383 7.37997160352774 8.00566891545219	

N 9.18093818089740 5.87368178915927 7.20334746608760  
 H 9.76437508526219 5.98603402891128 8.03789715483894  
 C 7.90899671372680 5.23100801370783 7.60148768528112  
 C 7.14131357895287 6.09950048243456 8.58463175098407  
 C 9.93666477287854 5.08192565736110 6.21355115176391  
 H 8.10309621331134 4.24195478453509 8.05351760733532  
 H 7.31383999334577 5.07268198788355 6.68808062009578  
 H 6.19149083824478 5.60152140679107 8.83967827674973  
 H 7.72075473714626 6.22097343605414 9.51577831601555  
 O 8.27649564079292 9.37146335373826 5.40574317597691  
 C 7.92332281038897 8.59681181010326 4.45691200477983  
 O 8.04218357599933 7.34452026546715 4.63755540032396  
 C 7.38997015535859 9.15810662812839 3.17246821914750  
 H 9.34993593473672 5.00113006598816 5.28837891780035  
 H 10.14397890974905 4.06865345029007 6.59707324504419  
 H 10.88764155185386 5.58525312144760 5.99158989849366  
 H 8.16879468253038 9.77680875604039 2.69875639883164  
 H 6.53192569103930 9.81397876670927 3.38684428874431  
 H 7.08674567126483 8.35771530648376 2.48572120490138  
 H 7.26136492558794 8.07244582988461 8.58275948141147  
 O 8.79555838039574 9.89454828948630 9.04602164565646  
 O 9.61856333811263 8.67315897405352 8.08642183412146  
 H 14.05430028280067 9.84834349222514 9.39970173941999  
 C 13.41605868900549 10.21940721014471 10.20549075297756  
 C 13.97072128736106 10.86884477672998 11.31258311487075  
 H 15.05195978676378 11.01276315596698 11.38618223404905  
 C 12.02665430621201 10.04014828990789 10.13096552684318  
 H 11.57658676274833 9.53091936415006 9.27475824892517  
 C 13.1392029084319 11.33852239065966 12.33729509138387  
 C 11.19524232843206 10.50870552077697 11.15270404111339  
 C 11.74627796982943 11.17177102725091 12.27803396529308  
 H 13.56977297901159 11.84694602416239 13.20527129945929  
 O 9.84097392302502 10.36055847623125 11.13995344897564  
 H 11.31307533118414 11.82162584282126 14.17169830010912  
 N 10.89363710872017 11.67926517106924 13.2574928843621  
 H 9.98497513064808 11.22799729964155 13.31179105075845  
 H 9.53454494867297 9.86846962984409 10.33886233413699

### <sup>3</sup>P<sub>1e</sub>

[Cu<sup>II</sup>(HMeEa)(OAc)OOH] + <sup>2</sup>OAP•, the latter is omitted  
 Cu 8.73132836902538 8.5884883777880 6.76344252890281  
 O 6.40001118609683 8.58415963090281 7.84754036358050  
 N 8.99622017376596 7.47096646705307 8.44677001201749  
 H 9.19865788780132 8.12133364413515 9.20221803216603  
 C 7.73964496426666 6.75960440595644 8.75503501450232  
 C 6.59730100939322 7.73264177314623 8.98175405866705  
 C 10.14217260511603 6.55128095479451 8.30965852154253  
 H 7.86424134790365 6.13556174384173 9.64692581179163  
 H 7.51691538421720 6.10337884353821 7.91209922608673  
 H 5.68119335559196 7.16496182729409 9.15546683719526  
 H 6.79156746841151 8.33961961347773 9.87108711144392  
 O 8.58902656390036 9.10409301982274 4.74617030129567  
 C 8.42297452242734 7.87522854742650 4.48295527546558  
 O 8.45426370560054 7.04031528040868 5.44129561690225  
 C 8.15908267476272 7.42017769045733 3.08037635938175  
 H 9.97052050230889 5.89014886120274 7.46190661842016  
 H 10.26796144529398 5.94847148078693 9.21313888344036  
 H 11.04794164841847 7.12909275997333 8.13351145755749  
 H 8.67111853051620 8.06326502436126 2.36629919879802  
 H 7.08431134009771 7.49425662213025 2.89334596798822  
 H 8.46049181167942 6.38304858535502 2.94588478495388  
 H 6.73739303617281 9.47013712854236 8.08562680611846  
 O 8.02863193384844 10.72580485369981 8.41340488122316  
 O 9.09269245909627 10.31211593274411 7.50951875495608  
 H 8.44189607428691 10.63896693116993 9.28626757560239

### Model [Cu<sup>II</sup>(HMeEa)(OAc)(OAP)] (multiplicity 2)

Cu 9.10407802492183 8.02329564887061 6.62224653800469  
 O 6.36351828781630 7.05076329204840 8.24760062017666  
 N 9.29852502118733 6.16678294748021 7.41998312334837  
 H 9.66801413546346 6.29980126125044 8.35981102499906

C 8.04824242838776 5.37523245945075 7.53628340802239  
 C 7.08761021593564 5.88586665873951 8.60098030701739  
 C 10.31622240819246 5.43956650244018 6.63045400648359  
 H 8.31969533898519 4.34488775098054 7.79339517502542  
 H 7.56339691883865 5.36240228727007 6.55946295240458  
 H 6.35640932221560 5.09418199186639 8.77878084829160  
 H 7.63626197757845 6.03735163134758 9.54019423308238  
 O 8.84345365985350 9.51059221261521 5.22107073867620  
 C 8.07773935468139 8.73442663462179 4.57081845867419  
 O 7.88694995286751 7.56240305467075 5.02229023705524  
 C 7.39324808271293 9.18999436561312 3.32008259901471  
 H 9.95719774292735 5.31933894566508 5.60915615458943  
 H 10.50502417737165 4.45192887606123 7.05890704145193  
 H 11.24393597234366 6.00852958743978 6.61718014323847  
 H 7.86675235484914 10.08389552672515 2.91969327134146  
 H 6.35132063890009 9.41856627422437 3.55861771858278  
 H 7.39742472131974 8.39231692548673 2.57757082731655  
 H 6.9660704980895 7.83462915863803 8.33913013254850  
 C 9.01806342342802 8.91817006377406 9.33933270464272  
 C 11.35765599637726 8.67456169746542 10.02559192759016  
 C 10.97942456524830 8.62967959902298 11.36502163806966  
 C 8.66375018778627 8.88218951499243 10.70195410571765  
 C 9.62843953804417 8.74166377570783 11.69090877931563  
 H 7.61360886474257 8.94833375060649 10.96198776437424  
 H 9.32215138689067 8.71054519771179 12.73039373476629  
 H 11.72693748148080 8.51242707154176 12.13881141065650  
 O 8.14149300069340 8.99209211309615 8.36357185995683  
 C 10.40073860660317 8.82694370858067 9.03520623498182  
 H 12.40246700061196 8.59201739003671 9.74585215854340  
 N 10.73052064873679 8.83326861163212 7.63213465317095  
 H 11.64237467313240 8.42287090671152 7.45784596530334  
 H 10.74796683906431 9.77883260561291 7.25411750356399

### Reaction F

<sup>2</sup>R<sub>1f</sub>  
 O -3.06636884776674 1.41204544050596 -0.27226466819199  
 C -4.23240876203327 1.93679033687411 0.22353452043444  
 C -5.43505695558716 1.05151417566500 -0.13112983267432  
 H -5.33499696651372 0.07476672806444 0.34701177650068  
 H -5.49594598264897 0.90453252403759 -1.21059079334464  
 H -6.36513580505831 1.50719722731672 0.21449041284371  
 C -4.13143197255995 2.18768596554236 1.73443715442929  
 H -5.04183999925609 2.66048481489433 2.10826519033226  
 H -3.2822815373557 2.83508221693190 1.95875082816801  
 H -3.99602420039925 1.24180432813514 2.26323192335733  
 C -4.34430488168042 3.30139755257687 -0.52911346247194  
 H -5.25941161830359 3.78681049695668 -0.18520890605119  
 H -4.40281695272918 3.14437663808892 -1.60556632917699  
 H -3.49110490172769 3.93882155440998 -0.29981781415464

### <sup>2</sup>TS<sub>1f</sub>

O 1.50835649044963 -0.79550473358825 -0.57216962020144  
 C 0.43502410365902 -0.47697247413091 -0.01426253581979  
 C -0.86006622270247 -1.14298140050003 -0.45824089832682  
 H -0.90246440592424 -2.12817315649248 0.01915091362555  
 H -0.86916872948944 -1.28951688065128 -1.53780387245830  
 H -1.74547148473138 -0.58622018777572 -0.15252495231657  
 C 0.46342617321926 0.00997871460475 1.42755173393775  
 H -0.43335140202342 0.56449861076894 1.70276235988870  
 H 1.34764527913456 0.61937769297017 1.61090113291643  
 H 0.51990726727977 -0.87469840057462 2.07145234649874  
 C 0.15510301558473 1.3913472577343 -0.95772363217697  
 H -0.78825889814725 1.68174140987719 -0.51293160834916  
 H 0.13390347088617 1.10132339489694 -1.99976092401952  
 H 1.03541534280506 1.92580016182187 -0.62640044319862

### <sup>2</sup>I<sub>2f</sub>

O -2.96859453491987 1.29895345384661 -0.20572984186259  
 C -3.99569434491262 1.39455996698578 0.43693123284238  
 C -5.31757154805991 0.91182428741334 -0.10287825262809

H -5.60741579931236 0.00368812314318 0.43598538376814  
H -5.24112663718625 0.68682321957049 -1.16535363726920  
H -6.10306563500897 1.65021101621308 0.07087214157331  
C -4.01485274722071 1.98530242713708 1.82288003423665  
H -4.59608552539591 2.91195720437244 1.81249624317686  
H -3.00352542750435 2.19523608034355 2.16716797604111  
H -4.51357449698629 1.30533885142331 2.51883462312280  
C -4.76128687065960 4.39032838629579 -0.93639114784838  
H -5.67531902083057 4.67022042545280 -0.43196926278207  
H -4.80302007281219 3.83043192783488 -1.85963325983485  
H -3.80572733919011 4.69118462996754 -0.53146223253612  
<sup>2</sup>CH<sub>3</sub>•  
C -4.76138792975655 4.39665427923297 -0.94047245748035  
H -5.67516500805954 4.66811491684400 -0.43060905002053

H -4.80342271584749 3.82794134365345 -1.85886402545356  
H -3.80537734633641 4.68945446026958 -0.52950946704555

**acetone**

O -2.97973346678453 1.35886395112573 -0.22968724281510  
C -3.9985652455167 1.40704802243388 0.43123293809654  
C -5.31535974550921 0.90355626186770 -0.10142576523199  
H -5.61908638695005 0.01957220814846 0.46792891373638  
H -5.23142777212390 0.64262552428697 -1.15513860496904  
H -6.09803814787750 1.65353212316128 0.03868202674367  
C -4.01363006514853 1.97615178361554 1.82645777850200  
H -4.56992959412289 2.91885914681362 1.82182614421575  
H -2.99998068365937 2.15947228738372 2.17909750416239  
H -4.53546561327233 1.30421169116309 2.51223130755939

**Listing S4.** Cartezian coordinates of the <sup>3</sup>I<sub>1a</sub> intermediate optimized using different functionals, ma-def2-TZVP basis set and tight integration grids in methanol (C-PCM model).

#### wB97X-D4

O 4.07478242994017 1.90345067597695 9.72808925337158  
N 2.09776922452465 0.78786848845114 8.26385888393037  
C 3.94675071310489 2.34278555716324 8.43456112826286  
C 2.93781479153894 1.73725783706654 7.67151849140608  
C 2.77149183231228 2.15173260265742 6.35259191309639  
H 1.99254894663847 1.68714366163883 5.75485414156305  
C 3.58201372741536 3.14058614495314 5.80246712806524  
H 3.43122968383631 3.44434954722667 4.77197154518012  
C 4.57774533669374 3.73023678317609 6.56875338229185  
H 5.21600844075922 4.50031948115462 6.14962240673430  
C 4.75748810945046 3.32501588392753 7.88966259800672  
H 5.53219385808677 3.77249534040255 8.50637763085258  
H 1.67005179227964 0.15495229953940 7.60293912557216  
H 2.52511699653492 0.28601068531266 9.02915313803534  
O 2.86099251557511 -0.46135101255512 11.77916398301444  
O 3.55156361129912 0.20497429696730 12.49194546361356  
H 4.80498799000965 2.36595172694088 10.15613978700283

C 4.75717138901714 3.32702506873555 7.89099617430979  
H 5.52906901540667 3.77507786070210 8.50754945766894  
H 1.65124230347845 0.15920585651592 7.61300294974168  
H 2.50238203548007 0.29992702453787 9.04784467390439  
O 2.89168147780949 -0.48884903403374 11.75940085305607  
O 3.54563916320576 0.22479715791234 12.47424864111766  
H 4.80164791747015 2.36601876326143 10.16665150544768

#### M06-L

O 4.10653743120979 1.95043347458258 9.69312865140247  
N 2.13193106941372 0.82418735729023 8.27126434766329  
C 3.96948556828615 2.37905303766860 8.40389984234593  
C 2.95635118691690 1.75826505952669 7.65675919156138  
C 2.77814609539383 2.15919425474930 6.33512615167738  
H 1.99969942725628 1.68170876550538 5.75102815710569  
C 3.57536480916148 3.14579566020839 5.76941208683683  
H 3.41438110746880 3.43603932682677 4.73906333848323  
C 4.57314902084878 3.74958407957168 6.51903609217456  
H 5.20129104442483 4.51733732433789 6.08686697244982  
C 4.76724140179193 3.35945477168622 7.83997778051634  
H 5.54314265288217 3.81458284591518 8.44550889564683  
H 1.68994580917573 0.17923717185356 7.63497291951243  
H 2.56616687179051 0.33851135367194 9.04114239546257  
O 2.78140805508028 -0.61156039450552 11.91627372803610  
O 3.43770839882634 -0.02893896748868 12.74148294446640  
H 4.83860005007210 2.42089487859956 10.10872650465803

#### PBE

O 4.14243565016687 2.08192026255684 9.81471545644280  
N 2.12902791340817 0.88883098931304 8.46334409288473  
C 3.99408570616374 2.43638024287402 8.49523291588648  
C 2.95762816704816 1.77733428984998 7.79055676925983  
C 2.77194253431831 2.10019684726318 6.43630904159278  
H 1.97758393287891 1.59245921196519 5.88352874092132  
C 3.57858673595323 3.04773404067509 5.80272599040574  
H 3.41058456553308 3.27919585216791 4.74947357663916  
C 4.59704254225471 3.69168967282786 6.51197688606005  
H 5.23341097679168 4.43139906139862 6.02414804555795  
C 4.80157400796191 3.37889141722419 7.86080848512897  
H 5.59472924082095 3.86733652569605 8.43345015634121  
H 1.62750849997256 0.22969913761875 7.87266270095820  
H 2.53489990677660 0.45011920760483 9.28744938039695  
O 3.26410762195629 -0.72911728382723 11.22040979465049  
O 2.81798270402920 -0.02112167349149 12.11390451262134  
H 4.89741929396519 2.57083219828294 10.19297345425114

#### BP86

O 4.04750587824008 2.13799104462984 9.81125287437844  
N 2.05667897884087 0.94242193858166 8.42334269311292

C 3.94468949579479 2.46629777296582 8.47771099523636  
C 2.91968640435394 1.80862586288175 7.75653001727501  
C 2.77733513521971 2.10788814181348 6.39167298913439  
H 1.99127231813971 1.60242243944637 5.82571780791514  
C 3.61873085604812 3.02970013744814 5.76220298774360  
H 3.48492862772437 3.24170889075211 4.70024993958311  
C 4.62715595274900 3.67141909295052 6.48774959339815  
H 5.28979333967839 4.39040525311443 6.00453959245861  
C 4.78662692005276 3.38297684858704 7.84919354231772  
H 5.57061583903301 3.87010051622951 8.43479892929227  
H 1.58004647768333 0.26771718640464 7.82930502164629  
H 2.43981799394428 0.51585727354363 9.26420556176776  
O 3.48622052427601 -0.80383683999133 11.42784568252701  
O 2.90872734222460 -0.17735553420727 12.30505691654649  
H 4.80071791599658 2.61943997484946 10.20229485566595

#### TPSS

O 4.19742232363425 1.92914525371619 9.72879762627280  
N 2.14601567958673 0.82036226588625 8.35692488295953  
C 4.01734037158449 2.36427610279379 8.43141589982842  
C 2.96672153591914 1.75245479202973 7.71610311540049  
C 2.74579707891413 2.16036111298377 6.39368614199584  
H 1.93984382155458 1.69271422530468 5.83224668847920  
C 3.53916354422444 3.14411900226403 5.79997699908258  
H 3.34551175203912 3.43934718460791 4.77241248063861  
C 4.57575862356277 3.73928123327648 6.52046507770797  
H 5.19992761027324 4.50346620695963 6.06661801435362  
C 4.81215684727445 3.34242550481954 7.84084001333179  
H 5.61669929710498 3.79076931731188 8.42058219410720  
H 1.66343653908603 0.18563563693688 7.72892600200886  
H 2.59441692276503 0.32427173383779 9.12033075515194  
O 3.42391596061597 -0.66462883701731 11.87712166605125  
O 2.59019788796575 0.15294215134464 12.22842815696458  
H 4.95622420389445 2.39683711294391 10.11879428566452

#### TPSSh

O 4.08373691245624 1.91504672692336 9.71850780591145  
N 2.10749065531734 0.79977475223688 8.26353304881120  
C 3.95482011230200 2.35501602230710 8.42334091777517  
C 2.94310155785093 1.74113226020762 7.66361409785568  
C 2.77453798980864 2.15323197880430 6.33942425820864  
H 1.99812070561900 1.68380855374949 5.74359394665537  
C 3.58161547960416 3.14449556571315 5.78565423070228  
H 3.42842266176887 3.44349933784683 4.75493633675668  
C 4.57885118416683 3.74227344414233 6.54976296654443  
H 5.21331091228968 4.51274156318883 6.12776666061441

C 4.76266989182316 3.34040625315788 7.87329045528596  
H 5.53686277664240 3.79078506531827 8.48726968723217  
H 1.66778032093963 0.15908027925289 7.61576754945565  
H 2.52568412264814 0.31262879946857 9.04557131175079  
O 2.83317273524491 -0.53849653744842 11.84593613316248  
O 3.52355715170085 0.13717984202130 12.56956719618029  
H 4.81681482981687 2.38117609310945 10.14613339709675

#### B97-3c

O 4.63568005273935 1.76308946484112 9.57227027163426  
N 2.50407599840979 0.59732553260155 8.38757268064383  
C 4.23684064596065 2.27959307495367 8.37047186325515  
C 3.14643271045844 1.64466213291965 7.75090507411896  
C 2.71101976740651 2.14210516860897 6.52279659252209  
H 1.87430294061351 1.65761659027981 6.03663012847594  
C 3.32923247498471 3.23199798650784 5.92647754279748  
H 2.96934489528865 3.59309850590762 4.97340986775804  
C 4.40448205010227 3.84922363080310 6.54933986204476  
H 4.89498516556390 4.69714226501819 6.09364086269677  
C 4.85459240637227 3.36526857552703 7.77280746429801  
H 5.69396763990787 3.83084612144859 8.27371734747116  
H 1.96805761280173 -0.00544778478873 7.78846728253640  
H 3.06199469385469 0.08601426934271 9.04802544337725  
O 2.67673640889172 -0.42127822038922 12.13731414009385  
O 1.96589560215380 0.51335821936516 11.85687690240247  
H 5.40290893448959 2.24916446705262 9.89294667387247

#### PBE0

O 4.07929832699618 1.91154851192394 9.71458677156763  
N 2.11334214867880 0.79699213302122 8.26033648370238  
C 3.95080799683241 2.34731870710269 8.43060627133912  
C 2.94213143832491 1.73756260250995 7.66939571500733  
C 2.77697459033737 2.15074455935813 6.34987503492021  
H 2.00044922707696 1.68248730806133 5.75292386306176  
C 3.58250467625508 3.13902601696785 5.79915010220231  
H 3.43060042085092 3.43953049301154 4.76861673742645  
C 4.57561652072956 3.73299368093086 6.56282169323881  
H 5.21120934757585 4.50371103983117 6.14287027539088  
C 4.75592111445477 3.32991726642424 7.88180540968152  
H 5.52958872604821 3.77958772222853 8.49751050362071  
H 1.66606102640061 0.16464381471867 7.61392865234383  
H 2.52212363191534 0.31162974645014 9.04480673863182  
O 2.85278002693430 -0.49963245676606 11.80432101016859  
O 3.53369791943258 0.17101656094288 12.51638477618601  
H 4.80744286115584 2.37470229328277 10.14372996151006

**Listing S5.** Cartesian coordinates of the <sup>3</sup>TS<sub>1a</sub> transition state optimized using different functionals, ma-def2-TZVP basis set and tight integration grids in methanol (C-PCM model).

#### $\omega$ B97X-D4

O 1.07678213676368 -0.05106760266418 1.6781884321880  
N -1.09359865679980 -1.34000146608543 0.41532498645317  
C 0.67978393553969 0.27416784285926 0.45499230631377  
C -0.43958096789768 -0.36827853498228 -0.1958866054562  
C -0.81546786186317 0.0692154542198 -1.50520645837950  
H -1.66560318876471 -0.41219181037125 -1.97585185728191  
C -0.11404550750249 1.05027566424187 -2.12889007176624  
H -0.39796787918825 1.37674372061238 -3.12229389233806  
C 1.00059966742865 1.65382245994175 -1.48489431924410  
H 1.55221156081401 2.43289703789931 -1.99866108065250  
C 1.38559664015785 1.27079127506370 -0.22186801083734  
H 2.22902726193320 1.73283202605211 0.27728479588194  
H -1.86850267984407 -1.78505148494395 -0.05896134302449  
H -0.78624591976256 -1.73198598034267 1.34343491675657  
O -0.39948514617226 -2.24886921791114 2.83737161522971  
O -0.84185072349299 -1.22761977178036 3.55182223562589  
H 0.49834732865091 -0.69567964301110 2.13409599458993

#### M06-2X

O 1.07876429972928 -0.04869275233248 1.67769804414018  
N -1.09808026482536 -1.33688306053689 0.42746331763982  
C 0.68267505806154 0.27199489134291 0.46082099708484  
C -0.43748517924927 -0.37039615070236 -0.18536929967584  
C -0.81331577428305 0.06551926292836 -1.49184663192694  
H -1.66323085959763 -0.41560334569355 -1.95932088604158  
C -0.11338345956267 1.04588000129745 -2.11808276147082  
H -0.39940453814077 1.37010716564675 -3.10933435324865  
C 1.00148644380602 1.64934212370713 -1.47886691768936  
H 1.55152931818275 2.42563666462227 -1.99404695747897  
C 1.38840209277049 1.26710262174446 -0.21862039587931  
H 2.23129558247663 1.72542493167408 0.28078541267860  
H -1.87120499586632 -1.77344056209308 -0.06061055960617  
H -0.79708441742998 -1.76842721212299 1.34385831425745  
O -0.36116131073617 -2.21534160449354 2.83121728917917  
O -0.89486549860563 -1.18981100454423 3.45424068407843

H 0.51506350327013 -0.70241197044430 2.14001470395915

### B3LYP

O 1.06639004618864 -0.12749119033056 1.65788833220688  
N -1.14692629933606 -1.35453921349498 0.37472261919451  
C 0.65942600917923 0.25170393003174 0.46306043973183  
C -0.44131589335848 -0.38829855449432 -0.21905177204520  
C -0.77807316586137 0.04522018557007 -1.52892314356125  
H -1.60610324975543 -0.44028837499014 -2.03033067979452  
C -0.07320933747675 1.04645064335827 -2.13498523087949  
H -0.34034974969225 1.36798915007006 -3.13295174006434  
C 1.00829756661835 1.66615893901356 -1.46483293155143  
H 1.56246678148916 2.45388301228223 -1.95823925177064  
C 1.35750283601595 1.27601500633192 -0.19327872353062  
H 2.18046175235407 1.74216346653050 0.33246254021490  
H -1.89122932686699 -1.80174900736059 -0.14160090001060  
H -0.88233795530342 -1.79347355714939 1.26336746636718  
O -0.62501096439537 -2.32369716189712 2.97023128404772  
O -0.41345388241846 -1.11193995213479 3.40701450511384  
H 0.36346483261917 -0.50810732133645 2.33544718633127

### M06-L

O 1.06655910722824 -0.27560217003032 1.57848328297501  
N -1.11836548505746 -1.41373220828139 0.31090033599195  
C 0.67839432551776 0.17766701525187 0.43478405893758  
C -0.43986053907747 -0.42224059845755 -0.26976363073542  
C -0.79368098333689 0.06093459050953 -1.54646721478889  
H -1.62881056515268 -0.39995384583122 -2.05892321525634  
C -0.09194885609723 1.08701435057360 -2.11643307502269  
H -0.37254907685354 1.45015639633311 -3.09628403508218  
C 0.99753612637729 1.67717227685426 -1.43976907277782  
H 1.54315483208005 2.48425242735533 -1.91110063191167  
C 1.36569072699860 1.23550059270388 -0.19681030323254  
H 2.19906816578204 1.67605846435269 0.33470028218313  
H -1.86227536277057 -1.87421776168687 -0.18628340859884  
H -0.82429185334531 -1.82616899671669 1.19255179300841  
O -0.63408267303277 -2.16215415561977 3.09492038207067  
O -0.36731131193402 -0.92251389200948 3.39523269062463  
H 0.28277342267847 -0.55217248530098 2.48026176161501

### PBE

O 1.07830609761965 -0.22337845264184 1.60769842142137  
N -1.12788684580251 -1.41818191320950 0.31612316722760  
C 0.67393078946640 0.20489114598308 0.44740135050678  
C -0.43818296878954 -0.42598086283028 -0.26496947683360  
C -0.77677734585933 0.02929150247879 -1.56789743586906  
H -1.60343395230412 -0.45812516808961 -2.08900674793008  
C -0.07999927495884 1.06319605595567 -2.15103545764600  
H -0.35319252264504 1.40566941617877 -3.15005344742520  
C 0.99353807951549 1.69048925894631 -1.46187908964783  
H 1.53643432749037 2.50659448013729 -1.94123421186665  
C 1.35257406053546 1.27263196584206 -0.19743990794488  
H 2.17737752118211 1.73997735634964 0.34296050042443  
H -1.87335925448838 -1.88011796923674 -0.19861414001953  
H -0.88441948332644 -1.80009859849103 1.24311370691292  
O -0.71363829621011 -2.16081964632736 3.07669333787253  
O -0.28291359206990 -0.97174202685946 3.46164343126935  
H 0.32164266064472 -0.57429654418580 2.52649599954785

### BP86

O 0.07803145187602 -0.20386860801857 1.61597435779012  
N -1.13025796706829 -1.41258199900400 0.33255923191886  
C 0.67255209792332 0.21245122680298 0.44874467617223  
C -0.43821190447442 -0.42680914696736 -0.25823675299564  
C -0.77454837577114 0.01508355971995 -1.56758284036200  
H -1.59959196027060 -0.47766282680988 -2.08529867004734  
C -0.07673808974536 1.04334886321085 -2.15988330919623  
H -0.34768739519246 1.37543447122033 -3.16262755781948  
C 0.99574679357737 1.67846687255087 -1.47452152256463  
H 1.53915142805549 2.4895777558489 -1.96090145872872  
C 1.35260906783524 1.27369788213509 -0.20446334850111

H 2.17586020675957 1.74683449347989 0.33248399929962

H -1.87401736821270 -1.88018952507137 -0.17969322692209

H -0.88703911386975 -1.78858392942487 1.26387309083394

O -0.71675080898210 -2.14491275648947 3.07787860889178

O -0.29283922449880 -0.95022732738997 3.46377815026139

H 0.32373116205858 -0.55005902552938 2.51791657196927

### TPSS

O 0.109247503352186 -0.20726795929183 1.61320935649634

N -1.12425500666470 -1.40937853595386 0.33597566234794

C 0.67329803961084 0.21562542517607 0.44687968636133

C -0.43758420532768 -0.41809419957432 -0.25109902240368

C -0.78850429833183 0.03479173440313 -1.55163705908799

H -1.61597021136976 -0.45139283173858 -2.06129182077318

C -0.09676323525011 1.06493250480433 -2.14130894737404

H -0.37590485969563 1.40506494817605 -3.13386350984716

C 0.98282498129233 1.69077914090912 -1.46222032721211

H 1.52131616585693 2.50062933133895 -1.94541383423477

C 1.3501300865490 1.27651202288553 -0.19970473946180

H 2.1752722425849 1.74237655323886 0.33054080132850

H -1.86852107473270 -1.87140374609333 0.17434904109708

H -0.87014924722095 -1.80288976345526 1.25295611118125

O -0.67771106990689 -2.20558343804039 3.04361657072322

O -0.29255625009356 -0.99886731046074 3.43623008502722

H 0.35266293339848 -0.56583387632372 2.46148002802601

### TPSSh

O 0.107730891908226 -0.17137523059458 1.63745628971669

N -1.13814309683539 -1.37615300378578 0.35450338926314

C 0.66708397430490 0.23008723608409 0.45918123439259

C -0.4398887030852 -0.40064871778664 -0.23228586494580

C -0.78205756842973 0.04516571814433 -1.53666390520782

H -1.61174364468775 -0.43651520428107 -2.04149320276714

C -0.07996589323978 1.05698983028639 -2.13237922768350

H -0.35114856228287 1.39073151599003 -3.12651109268758

C 1.00334592376798 1.67313400798617 -1.45690473713324

H 1.55312538488853 2.46935192931984 -1.94431061533151

C 1.35963239133994 1.26890750506808 -0.19157223654735

H 2.18538755424657 1.73020995139665 0.33634958618074

H -1.88351750104950 -1.82548871622865 -0.16045540434989

H -0.88698439315918 -1.79050500906555 1.26353828632131

O -0.68039018620411 -2.25608652842995 2.97854616629769

O -0.34835530605111 -1.05773754071038 3.40333401867535

H 0.35631087461776 -0.55006774339298 2.38966731580632

### B97-3c

O 0.107556504353242 -0.25512127994266 1.57986378647985

N -1.12084247543692 -1.42373094446066 0.30380714983266

C 0.67518623672806 0.18175385146588 0.43004368004680

C -0.43736380695466 -0.43425068054237 -0.27278259708265

C -0.78240548778128 0.02903601456252 -1.56004925755014

H -1.60797000385007 -0.44330192709288 -2.07414866398014

C -0.08697730404845 1.05386085618604 -2.13875873032101

H -0.36303003838731 1.40046536800853 -3.12393522646342

C 0.9905489304141 1.66466222780814 -1.46028245316545

H 1.53073629435356 2.47072735677597 -1.93555129635669

C 1.35366174545940 1.24056015234985 -0.20973820657322

H 2.17827248699778 1.69587467385107 0.31951624983019

H -1.86394011603192 -1.87936651498675 -0.19476182801611

H -0.86468690269705 -1.80585322504371 1.20668970657050

O -0.67868795598545 -2.09009913010213 3.1687828604784

O -0.30772633287607 -0.87070588621981 3.44920979885508

H 0.30965372393655 -0.53451091261702 2.51209501984590

### PBE0

O 0.105957756204196 -0.13396378824038 1.65236566478623

N -1.14752197874199 -1.34184572030670 0.38836608372252

C 0.65644929895054 0.24994459239413 0.46238509763219

C -0.44026037894589 -0.38591843226057 -0.21468546746991

C -0.77697494799922 0.04334867927790 -1.52047382902063

H -1.60647651936752 -0.44330250195557 -2.02152470783627

C -0.07298472491139 1.04287163067333 -2.12786700132588

H -0.34182234316650 1.36248916035297 -3.12747336325554  
 C 1.00517558429336 1.66081082255730 -1.46153078629142  
 H 1.56166863783219 2.44804459456279 -1.95604162516724  
 C 1.35292939000709 1.27212966887344 -0.19100166613286  
 H 2.17722389503597 1.73810684602638 0.33573257376066  
 H -1.88892703160960 -1.79345415139391 -0.12649014755589  
 H -0.86015533570767 -1.79344076422928 1.26248141447400  
 O -0.58039784259299 -2.31594066071903 2.95435456239448  
 O -0.44264463455321 -1.11418849554285 3.37610597753596  
 H 0.34514136943486 -0.49569148006998 2.31529721974961

**Listing S6.** Cartesian coordinates of the  $^3\text{I}_{2a}$  intermediate optimized using different functionals, mdef2-TZVP basis set and tight integration grids in methanol (C-PCM model).

**wB97X-D4**

O 4.13017063658844 1.94372549601269 9.77293160796457  
 N 2.22869429772030 0.64590614188362 8.22045403887694  
 C 3.95817363877952 2.29043135398757 8.56927683143553  
 C 2.96860135851933 1.63336475071289 7.71632218224323  
 C 2.81080543279810 2.0529378635129 6.37023560038943  
 H 2.07128927430613 1.54958436147430 5.75583789518653  
 C 3.57379910543684 3.06542068992481 5.86866964514240  
 H 3.44590438095915 3.37947933933720 4.83880509698921  
 C 4.54345131416721 3.72119565418187 6.68460581376398  
 H 5.13587727683196 4.52410311671971 6.25947772796598  
 C 4.72682492978376 3.34865974474599 7.97997120203048  
 H 5.45930541140025 3.83649213809535 8.61374003529234  
 H 1.54066811702207 0.18533223345744 7.64550843636690  
 H 2.32401626773571 0.33648656858157 9.18131875155383  
 O 2.40670078437760 -0.37922285216864 11.06047876992184  
 O 3.35284341243847 0.34015280980051 11.60839663102113  
 H 3.66219436113483 0.97284058490161 10.87335973385504  
 N 2.24250225412155 0.65230840197871 8.23444337771958  
 C 3.96774542365686 2.30062601346856 8.57052272902391  
 C 2.97552101033789 1.63770246222028 7.71912665888180  
 C 2.81431741967122 2.04968861160393 6.38114201484180  
 H 2.07535450310698 1.54448326152883 5.77111672899649  
 C 3.57533475420898 3.06510488341293 5.87014433651361  
 H 3.44072171812870 3.37170097829299 4.84114211420295  
 C 4.53819651056879 3.72014314608895 6.67372863214808  
 H 5.12836457325975 4.52125118668753 6.24717768036112  
 C 4.72578730737843 3.35063563352381 7.97411553200143  
 H 5.45889161230616 3.84312518058972 8.60011552591030  
 H 1.55387784880134 0.18464096065649 7.66961948992569  
 H 2.34160439653879 0.34522067226928 9.19952800672516  
 O 2.38174930112443 -0.37889945611711 10.99707709577702  
 O 3.32206295993240 0.31820935709720 11.60372375947915  
 H 3.65504337261071 0.96239140797262 10.89291914666022

#### PBE

O 4.18185816669321 1.97281151885931 9.82341168887520  
 N 2.23686344065343 0.62853892287528 8.25426858979252  
 C 3.97984129055022 2.29660600340553 8.59862951558736  
 C 2.97858516465513 1.62299836912670 7.75182621997812  
 C 2.81032631987214 2.03800167445875 6.40257190059380  
 H 2.06254855044091 1.52511054502315 5.79344162614212  
 C 3.56987856312215 3.05924767860968 5.88077100374167  
 H 3.42824452444357 3.36661569411519 4.84373398225034  
 C 4.54186971888592 3.72063687777312 6.68463540451315  
 H 5.13441595320315 4.52872920865090 6.25220039049437  
 C 4.73661482783566 3.34945445302635 7.99486817462904  
 H 5.47761278022574 3.84766633635451 8.62239385408572  
 H 1.54656563970812 0.17388854922437 7.66158230155896  
 H 2.31284178664319 0.29398373279307 9.23129061991138  
 O 2.36263254430455 -0.36456722378306 10.94471145900751  
 O 3.32202486230418 0.36031882807813 11.52327405635010  
 H 3.65659586645836 1.02684883140877 10.75577921248791

#### BP86

O 4.18021738631961 1.97567113440883 9.82644748095299  
 N 2.23543417485234 0.62839056508149 8.25643134586120  
 C 3.97877111624025 2.29792222524603 8.59983871953843  
 C 2.97781117992790 1.62285990461952 7.7529508895539  
 C 2.81052493707188 2.03669668173923 6.40223373932189  
 H 2.06373294465367 1.52354699302125 5.79286880922435  
 C 3.57074017930173 3.05780312730357 5.88030793898899  
 H 3.43027960815831 3.36424957289614 4.84319465741316  
 C 4.54257644736135 3.72055614267758 6.68500526407684  
 H 5.13511755990490 4.52806325580870 6.25233100711546  
 C 4.73647090661024 3.35070742543318 7.99621596903639  
 H 5.47664990097559 3.84959305574838 8.62356900633277  
 H 1.54551103845307 0.17275896860597 7.66406670800910  
 H 2.31087031874606 0.29478055698197 9.23488513632492  
 O 2.36025630546407 -0.36334312665019 10.93819445512178  
 O 3.32550393580725 0.35756800333889 11.51926000223654  
 H 3.65885206015142 1.02906551373922 10.75158887058901

#### TPSS

O 4.17299432656325 1.97033617998752 9.81403618315920  
 N 2.23679978644237 0.63445829172424 8.25024106524782  
 C 3.97692791109219 2.29928919607645 8.59030456821110

**B3LYP**

O 4.14957667107073 1.95385289519490 9.78817888679165  
 N 2.23174528677838 0.64119079653899 8.23041411528368  
 C 3.96689895031527 2.29318183718429 8.57866536442013  
 C 2.97244979678175 1.63002782874308 7.72818486987290  
 C 2.81180847762846 2.04760290925746 6.38469544033852  
 H 2.07262070194514 1.54379350404329 5.77333969532100  
 C 3.57306476115038 3.06293851501321 5.87573838500516  
 H 3.44039137324137 3.37311912482144 4.84738746317246  
 C 4.54097059734214 3.71904574667455 6.68488770982745  
 H 5.13099341340562 4.52070695531415 6.25890600256513  
 C 4.72847741567942 3.34675713892448 7.98510613783467  
 H 5.46156147226257 3.83705589686222 8.61306091883002  
 H 1.54432495196659 0.18278487670963 7.65187297281306  
 H 2.31927470511073 0.32203522086890 9.19232290019413  
 O 2.39171610231555 -0.37358683016199 11.01544517721791  
 O 3.34289986207083 0.35302823620272 11.57686737516618  
 H 3.66054546093467 0.99335534780844 10.83431658534523

#### M06-L

O 4.14224503424666 1.95855729872503 9.77374717083095

C 2.97871704475080 1.62825130933379 7.74407598397936  
C 2.81071588561787 2.04060548121866 6.39564272287821  
H 2.06723117067382 1.53040884416772 5.78841344348780  
C 3.57110497553687 3.06026024018494 5.87639524114587  
H 3.43258517490368 3.36665676102032 4.84395557201375  
C 4.54213254090390 3.72161615890797 6.68141200291764  
H 5.13214193192323 4.52550904629796 6.25041663177977  
C 4.73542467206935 3.35190703029543 7.99002754849843  
H 5.47240151299552 3.84788510039882 8.61503565820027  
H 1.54733545062259 0.17623660094648 7.66556544712283  
H 2.31907440855501 0.30720036209970 9.22201081965492  
O 2.36425528621149 -0.37499951162618 10.95976336591699  
O 3.32604247509079 0.35218957831568 11.54437452407997  
H 3.65343544604690 1.00907933065027 10.78771922170537

#### TPSSh

O 4.16055312071879 1.96098461927561 9.79842266821884

N 2.23809611645560 0.63959928710179 8.24201662987921  
C 3.97180766437369 2.29568432749293 8.58364195804776  
C 2.97711971603621 6.2982863780917 7.73670462065895  
C 2.81127838410138 2.04355947621162 6.39176171298730  
H 2.07009075139731 1.53646078838937 5.78360067352475  
C 3.57121514515603 3.06034201196533 5.87805551879308  
H 3.43533918088669 3.36860085999427 4.84836222961418  
C 4.54016623219828 3.71859571504388 6.68429128268659  
H 5.12948448797270 4.52096966096938 6.25570685625428  
C 4.73110498527654 3.34804250840965 7.98755335226621  
H 5.46582206747989 3.84084169727194 8.61350178891577  
H 1.54965249617100 0.18049244647200 7.66275943776843  
H 2.32534230173027 0.31871214346452 9.20877963063323  
O 2.37786910979069 -0.36881646829688 10.97893622875933  
O 3.32987232777884 0.35298453574092 11.55524728988688  
H 3.65450591247569 1.00000775268424 10.81004812110448

#### B97-3c

O 4.17548008567705 1.96653208062720 9.80060601940506

N 2.24154128008143 0.63862290023964 8.24078778162695  
C 3.97637564915328 2.29357752901605 8.58729459199311  
C 2.98006544802470 1.62754547481257 7.74362873596828  
C 2.81347366916562 2.04341191144048 6.40493876054997  
H 2.07320263301236 1.53921858819136 5.79870348038879  
C 3.56889091557910 3.05785788728559 5.88930601042658  
H 3.42898388414151 3.36477426738881 4.86306588868955  
C 4.53588319641765 3.71260699265118 6.68926368175362  
H 5.12308542928876 4.51305278546441 6.26205264672626  
C 4.72972680830009 3.34171551415099 7.98860429676744  
H 5.46479860133609 3.83425335661443 8.60900359257469  
H 1.55742458798261 0.18776356435009 7.65967739217763  
H 2.32169846356287 0.30879611519353 9.20086564781804  
O 2.38067632686194 -0.36811921894256 10.97491724275397  
O 3.32144609794034 0.37135785049422 11.53343363692624  
H 3.64656692347420 1.01392240102180 10.77324059345305

#### PBE0

O 4.14635665344087 1.95348936601276 9.78521590526466  
N 2.23727289500871 0.64520682807967 8.23483352649145  
C 3.96466696117111 2.29081190740724 8.58132860901254  
C 2.97383950246318 1.62936957957139 7.73279557471805  
C 2.81310907182764 2.04438431530449 6.39140169426229  
H 2.07320457927319 1.53862296654652 5.78015328031162  
C 3.57232642038332 3.05754433608773 5.88317566440153  
H 3.43938583490233 3.36711785588249 4.85329161893985  
C 4.53727738287498 3.71304851024304 6.69068678645817  
H 5.12799339444952 4.51586861032671 6.26449296091448  
C 4.72407798922542 3.34234165889211 7.98843956931260  
H 5.45747388599469 3.83370658880102 8.61749919206196  
H 1.55067172355219 0.18698844614977 7.65654145804788  
H 2.32595601861127 0.32874008374090 9.19868718298424  
O 2.39674921132112 -0.35351929909426 10.99134997426515  
O 3.33829722408238 0.35448073056581 11.55202452857663  
H 3.66066125141772 0.99868751548236 10.81747247397621

**Listing S7.** Cartesian coordinates of the  ${}^3\text{TS}_{1e}$  transition state optimized using M06-2X functional, ma-def2-TZVP basis set and tight integration grids in methanol (C-PCM model).

Cu -0.24447799027672 1.16565920517684 -1.36118876057909  
O -2.22570329850125 0.88681533085613 -0.22502882873537  
N 0.07942472077819 -0.73719119011226 -0.67670844351338  
H 0.65111826235656 -0.62086911848572 0.15989899193997  
C -1.22511447492742 -1.29076188167194 -0.27038832589492  
C -1.99274023232875 -0.28599225870231 0.5599258252952586  
C 0.79609171365544 -1.63455653396507 -1.59488306146364  
H -1.09014267299008 -2.21699774882654 0.29707653464977  
H -1.78411940868078 -1.52193465115838 -1.18025130089889  
H -2.94408884907757 -0.71752532432180 0.87482443529563  
H -1.42218058536722 -0.01325892579667 1.45073550032918  
O -0.66795627731790 2.80376724840182 -2.50719070028069  
C -0.96358089578998 2.02519265506006 -3.46037241909164  
O -0.84198475296716 0.77733613373007 -3.27963003304915  
C -1.42099838796091 2.57401677324811 -4.77426382511466  
H 0.23538235346438 -1.71196965553164 -2.52531955475464  
H 0.90789989664306 -2.62911291679593 -1.15556868517789  
H 1.78081801026821 -1.22028720025205 -1.80392215403598  
H -2.05320227465864 3.44468622772139 -4.61384658684412  
H -1.94425206871585 1.81457983769846 -5.34842413314211  
H -0.53766352023486 2.89461555910915 -5.33029171068963  
H -2.07865860549659 1.65610272276322 0.34974123340192  
O -0.39033759494537 2.46101725934438 1.11546066705781  
O 0.54777342335873 2.03706800510329 0.22053013577921  
H 3.85585375587836 -0.57893281765765 0.77609950953625  
C 2.94500867998215 -0.68427390833133 1.35023097661284  
C 2.40978633736327 -1.95438747116164 1.59317403514326  
H 2.90591480860786 -2.83227922812784 1.19865882407565  
C 2.29935416080374 0.43451815470015 1.84037224566060